"INVESTIGATION OF THE HETEROPOLY COMPOUNDS OF TITANIUM-TUNGSTEN AND (FERRIC) IRON-TUNGSTEN."

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PART 1.

THE TITANIUM ANALOGUES OF THE TUNGSTO-SILICIC ACIDS AND THEIR DERIVATIVES.

Introduction.

In the course of work on the analytical separation of titanium from tungsten it was found that, contrary to expectation, no complete separation could be effected in acid solution. A similar observation has been recorded by Schoeller[1], who found that under certain circumstances a pyro--sulphate fusion of a mixture of titanic oxide and tungstic oxide gives a melt which is completely soluble in water, there being no separation of tungstic oxide. This anomalous behav--iour of tungsten in presence of titanium suggested that at some stage of the separation a water-soluble compound contain--ing both titanium and tungsten was being formed. Considering the position of titanium in the Periodic Table, the most probable compound would be one of heteropoly-tungstate type analogous to the tungsto-silicates, and the present investigation records attempts at its isolation and characterisation.

Historical Survey.

Compounds having the formulae $TiO_2.12WO_3.xH_2O$ and $TiO_2.10WO_3.xH_2O$ were prepared by R.Lecarme according to D.Klein[2] using methods previously employed by C.Marignac[3] for the tungsto-silicic acids $SiO_2.12WO_3.xH_2O$ and $SiO_2.10WO_3.xH_2O$. The free acids were isolated by decomposition of the mercurous salts with hydrochloric acid, excess mercury precipitated with sulphuretted hydrogen and the filtrate concentrated in a vacuum desiccator.

The existence of these compounds could not be con-
-firmed by L.-A.Hallopeau.[4]

Extensive work had already been carried out on the tungsto-silicic acids and their salts. The methods of preparation and analyses used in the following work is naturally based upon and follows closely the methods used in investigation of the tungsto-silicic compounds.

C.Marignac[5,6,7] isolated the first tungsto-silicate; it crystallised from the mother liquor of an ammonium tungstate solution containing silicic acid. A.Laurent[8] had probably already prepared tungsto-silicate compounds and describes them as polytungstates.

The Nomenclature.

The nomenclature is due to A.Rosenheim and J.Jaenicke.[9]

The known tungsto-silicic acids are:-

1. $4H_2O.\ SiO_2\ .12WO_3\ .28$ or $22H_2O$ or $H_8\left[Si(W_2O_7)_6\right].28$ or $22H_2O$.
i.e. 12-tungstosilicic acid.

2. $4H_2O.\ SiO_2\ .10WO_3\ .\ 3H_2O$ or $H_8\left[Si\overset{O}{\underset{}{\backslash}}(W_2O_7)_5\right]3H_2O$.
i.e. 10-tungstosilicic acid.

3. $4H_2O.\ SiO_2.12WO_3.20H_2O$ or $H_8\left[Si(W_2O_7)_6\right].20H_2O$.
i.e. iso-12-tungstosilicic acid.

The Constitution.

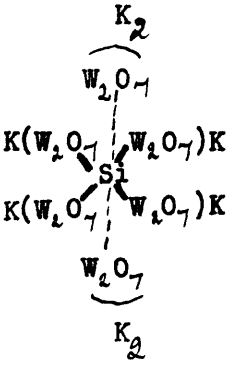
Owing to the size of molecules of heteropoly compounds, differences of a fraction of a percent correspond to a considerable variation in molecular formula. It has been found that the constitution can be definitely settled only by X-ray analyses of the crystals. Even then the structures in solution may be different from those found in the solid state.

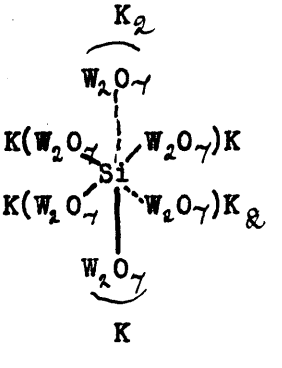
Miolati's[10] suggested theory (based on Werner's Co-ordin-

-ation Theory) has been successfully developed by A.Rosenheim[11] to include most of the heteropoly compounds.

According to Miolati[10], the central atom (e.g. P, As, I, Si, etc.) is hydrated and attached to six oxygen atoms e.g. H_8SiO_6, and the oxygen atoms can be wholly or partially substituted by radicles such as WO_4, MoO_4, W_2O_7, Mo_2O_7, etc., to form such compounds as $H_8\left[Si(W_2O_7)_6\right]$; $H_8\left[SiO(W_2O_7)_6\right]$; $H_8\left[SiO_2(W_2O_7)_4\right]$. When the co-ordination number is six, the series of compounds is known as the "limiting series" and if the whole of the oxygen is replaced, as "saturated series"[11]. The existence of double radicles (W_2O_7 and Mo_2O_7) is doubtful, and was postulated to explain the six co-ordination number.

The separation into isomers was explained by Rosenheim and Jaenicke[12], thus:-





An alternative hypotheses of constitution assumes silicic acid formulated as follows:-

$Si(OH)_4.2H_2O$ or $Si\begin{matrix}(OH_2)_2\\(OH)_4\end{matrix}$, which can be written $H_8\left[Si\begin{matrix}O''_2\\O'_4\end{matrix}\right]$.

By addition of $12WO_3$ groups to this acid, there would be produced a compound containing bivalent and monovalent oxygen: $H_8\left[Si\begin{matrix}O''_2\\O'_4\end{matrix}.12WO_3\right]$ which admits of a cis- and trans- isomerism (P.Pfeiffer[14]).

Copaux[15] first proposed the use of two hydrogen atoms as a nucleus. If a molecule of water is taken as $(H_2O)_6$, by isomeric change it can give $H_{10}\left[H_2(O)_6\right]$, called "aqua acid". Then the oxygen atoms may be replaced by the radicles Mo_2O_7 or W_2O_7 as before, and the outside hydrogen ions by the metals. The conception is artificial but useful to clarify the structure of, for example, the metatungstates.

The most usual formulae for acids are those already used in the nomenclature: $H_8\left[Si(W_2O_7)_6\right].28$ or $22H_2O$ and $H_8\left[SiO(W_2O_7)_5\right].3H_2O$ and are due to Rosenheim and Jaenicke.

The true constitution of the 12-heteropoly acids and meta-tungstates in the solid state has been shown by the X-ray crystal analyses carried out by Keggin[16], and based on the work of L. Pauling[17]. In the 12-heteropoly acids and metatungstates the polyacid ions may be regarded as co-ordination structures, built up of polyhedra of oxygen ions. Compounds of the first type are represented $R_3H\left[Si\,W_{12}O_{40}\right]aq.$, and of the second: $R_6\left[H_2Mo_{12}O_{40}\right]aq.$

The similarity between the paratungstates and 6-heteropoly acids led to their formulation by Rosenheim[18] as $R_5H_5\left[H_2(WO_4)_6\right].aq.$

J.H. Sturtivant[19] has recently shown that ammonium paratungstate is correctly represented by the older formula $3(NH_4)_2O.7MoO_3.4H_2O$ or $(NH_4)_6\left[Mo_7O_{24}\right].4H_2O$; it may be with MoO_6 as nucleus of the structure (Anderson[20]).

Basicity.

The problem of basicity is much disputed in the literature. According to Marignac[21] all these acids are 8-basic. The normal 12-tungstosilicic acid gives the 4-basic (acid) and 8-basic (neutral)

salts.[22] Wyrouboff describes similar types of salts, neutral and basic. The best defined are the so-called 4-basic salts.

Conductivity measurements during neutralisation of the free acids with alkali points to the existence of 4-basic salts only; even onductivity measurements of the free acids correspond to those of 4-basic acids according to Copaux,[23] and the neutralisation curve of Malaprade.[24]

Yet on the ground of the Miolati-Rosenheim theory,[9,10] the 8-basicity is accepted.

According to Scroggie and Clarke,[31] no normal potassium tungstate is split off by the addition of 8, 9 or 10 equivalents of potassium hydroxide to one molecule of 12-tungstosilicic acid $H_8[Si(W_2O_7)_6]$. 11 equivalents of potassium hydroxide gave some potassium tungstate K_2WO_4, as was shown by precipitation of hydrat--ed tungstic oxide on addition of acid. 12 equivalents gave un--doubted evidence of decomposition. From these results it is apparently possible to prepare 8-basic salts of the acid $H_8[Si(W_2O_7)_6]$.

There exists an 8-basic guanidine salt $(CN_3H_6)_8[Si(W_2O_7)_6]$. $6H_2O$. (R.Haeberle).[25]

The 8-basic salts are not the principal salts (Copaux)[26] but the double basicity is accepted and the formula is often written $H_4H_4[Si(W_2O_7)_6] \cdot xH_2O$.

Keggin[16] has shown from the crystal structure that the basicity in the solid state is four for 12-tungstosilicic acid.

Preparation of 12-tungstosilicic acid. $H_8[Si(W_2O_7)_6]28$ or $22H_2O$.

The classical method of preparation of the free acid is through the mercurous salt which is precipated from the solution of

the sodium or potassium salt. The latter is prepared by boiling a solution of sodium or potassium paratungstate with gelatinous sil-icic acid. Last traces of mercury are removed from the filtrate by precipitation with sulphuretted hydrogen which does not attack the complex acid, after the free acid has been obtained by decom-posing the mercurous salt with hydrochloric acid. The free acid crystallises from the solution in large shining colourless crystals (Marignac[3]). The compound was also prepared by the same method by Wyrouboff[24], the starting material being prepared in the following way:

A hot solution of normal sodium tungstate in three or four times its weight of water, was treated with freshly precipit-ated gelatinous silicic acid and small quantities of nitric acid. The filtered solution was treated with mercurous nitrate, when the mercurous salt of 12-tungstosilicic acid was precipitated. Subsequent treatment of the mercurous salt following Marignac's method[3] was carried out in order to avoid excess of hydrochloric acid. If, instead of precipitating the complex acid with mercurous nitrate, the dilute solution of nitrates is shaken with ether and sulphuric acid, an ether addition compound of theacid falls to the bottom of the solution as an oily layer. On careful evaporation of the ether-oil, beautiful crystals of the acid are obtained (E.Drechsel[28] and Copaux[29]).

This method was modified by E.O.North and G.D.Beal[30] who combined and varied the methods of Marignac[3] and Dreschel[28] in their method of preparation:

To a boiling solution of sodium paratungstate, prepared by the neutralisation of hydrated sodium tungstate ($Na_2WO_4 \cdot 2H_2O$) with

hydrochloric acid, freshly precipated silicic acid gel and excess hydrochloric acid in small quantities were added, until the solution was faintly acid. As soon as a sample of the boiling solution ceased to be turbid when treated with concentrated hydrochloric acid, the excess silicic acid gel was filtered off, and the filtrate shaken with ether and hydrochloric acid. According to Scroggie and Clark[31], this method gives an impure acid. A.Rosenheim and J.Jaenicke[32] produced the compound from normal sodium tungstate and a slight excess of sodium silicate reacting in acetic acid solu-tion. Here the product was contaminated with iso-12-tungstosilicic acid. Purification of the crude product was effected by addition of the calculated quanity of potassium carbonate, when the potassium salt of the normal acid was obtained by fractional crystallisation, the potassium salt of the normal acid being less soluble than that of the iso-acid. The yield was four fifths normal form and one fifth iso-form. The pure acid was then prepared by shaking with ether and sulphuric acid (H.Copaux[33]). According to North and Beal[30] there is often slight reduction of the tungstosilicate in solution by the acetic acid. Metatungstic acid does not react at all with silicic acid gel to give the complex acids (L.Malaprade[34]).

The 12-tungstosilicic acid crystallises in large colourless or sometimes light yellow crystals; the crystalline form being tetragonal, pseudocubic or octohedral. The 28-hydrate is isomorphous with boro- and phospho-tungstic acids and silico-and phospho-molybdic acids (A.Rosenheim, J.Jaenicke[35]). The isomorphism with borotungstic acid was shown by D.Klein[36].

Preparation of 10-tungstosilicic acid $H_8[SiO(W_2O_7)_5] \cdot 3H_2O$.

This acid is difficult to prepare pure.

It has been prepared from the ammonium salt of the acid. The ammonium salt is prepared by boiling ammonium paratungstate with gelatinous silicic acid. By addition of mercurous nitrate or silver nitrate in the cold, an insoluble precipitate is formed. The precipitate when treated with hydrochloric acid (care being taken to avoid an excess) filtered, and the filtered solution evaporated in vacuo, gives a final product which is slightly contaminatedwith the ammonium salt. Better results are obtained through the silver salt, when it is precipitated with excess silver nitrate (Marignac).[4,37] The filtered solution when concentrated becomes syrupy and then forms a transparent light yellowish glass. The proportion of water lost at 100° is in accordance with the formula $H_8[Si^{O}(W_2O_7)_5] \cdot 3H_2O$. (C.Marignac).[37] The free acid may also be obtained from the ammonium salt by extraction by the Drechsel method.[28] By boiling a solution of 50 grams of ammonium paratungstate in 500 ml water with gelatinous silicic acid, a compound was produced containing silica and tungstic oxide in the ratio $SiO_2 : WO_3 :: 1:7$. Doubtless this was contaminated with colloidal silicic acid, according to Rosenheim and Jaenicke.[38] Experiments of transition of the 12-acid to the 10-acid through the action of varying strengths of base (sodium bicarbonate, sodium carbonate, ammonium bicarbonate, potassium bicarbonate, barium carbonate) in quantitative amounts gave no definite intermediate products, (Rosenheim and Jaenicke).[39]

According to Scroggie and Clark,[31] however, 14 equivalents

of alkali (potassium hydroxide) gave the 10-acid: $2H_2O.SiO_2.10WO_3.5H_2O$

18 equivalents gave the 8-acid: $2H_2O.SiO_2.8WO_3.4H_2O$

20 equivalents gave the 7-acid: $2H_2O.SiO_2.7WO_3.4H_2O$

Further addition of alkali caused complete decomposition.

Metatungstic Acid $H_{10}[H_2(W_2O_7)_6].22H_2O$ - the Parent Acid.

Metatungstic acid, with the above formula, was prepared and analysed by A.Rosenheim and J.Jaenicke.[40] This formula shows it to be isomorphous with 12-tungstosilicic acid $H_8[Si(W_2O_7)_6].22H_2O$. In physical and chemical properties, metatungstic acid and its derivatives are so similar to the substituted heteropoly compounds as to be inseparable from them if mixed. There is always a strong possibility, therefore, that the patent acid meta-tungstic acid, will be produced during the preparation of the substituted acids.

Margueritte[41] observed that the product of fusion of tungstic oxide (WO_3) with alkali carbonate (neutral tungstate) gave on treatment with hydrochloric acid, added very gradually, hydrated tungstic oxide, which at first redissolved in the undecomposed tungstate. On carrying the addition of hydrochloric acid further, the hydrated tungstic oxide ceased to redissolve. On filtering the acid liquid and treating with zinc, tungstic oxide was found to be present. After concentrating, and removing repeated crops of alkali chloride, a very small amount of a product, water soluble and containing alkali and tungstic oxide, was obtained. This was undoubtedly sodium metatungstate: $Na_2O.4WO_4.xH_2O$. Further he observed that similar treatment of neutral tungstate with hydro-chloric acid in the cold gave a precipitate of hydrated tungstic

oxide, redissolving on heating. He then went on to the usual prodedure of saturating neutral tungstate with hydrated tungstic oxide and prepared a variety of acid tungstates.

Meanwhile Scheibler[42] had in an extended research prepared a great number of metatungstates and had discovered their outstanding characteristics.

Possible methods of preparation of Metatungstic Acid.

1. When alkali paratungstate solutions are allowed to boil with excess of pure hydrated yellow tungstic oxide until a filtered sample gives no precipitate of tungstic oxide on treatment with hydrochloric acid (H.Copaux)[43], and the filtered solution is con-centrated to some extent by boiling and finally evaporated over concentrated sulphuric acid, crystallisation of alkali meta-tungstate takes place.

2. When a saturated alkali paratungstate solution is treated with a large excess of concentrated acetic acid a heavy oily layer falls to the bottom. This is concentrated metatungstate solution, (Scheibler)[42].

3. Margueritte[41], by adding dropwise a strong mineral acid to boiling paratungstate solution as long as the resulting precipitate was redissolved, produced metatungstates in solution. This method has not been generally used for the preparation of metatungstates owing to the necessity for removal of the mineral salts formed concurrently.

4. By means of electrolysis of alkali tungstate solution using a cell with a diaphragm, it is possible to enrich the anodic liquid in WO_3 to the extent necessary for metatungstate formation.

5. According to V.Knorre[44] heating of sodium paratungstate ($3Na_2O.7WO_3$)

solution causes partial decomposition in to normal sodium tungstate and sodium metatungstate.

$3(3Na_2O.\ 7WO_3) \rightleftharpoons 5Na_2WO_4 + 4(Na_2O.4WO_3)$.

The reverse action taken place only incompletely on cooling.

The free acid can be prepared from the salts in the following ways:

(a) By treating the ammonium salt with chloroplatinic acid (Laurent[45]).

(b) By treating the barium salt with sulphuric acid (Scheibler,[42] Péchard,[46] Malaprade[47]).

(c) By treating the lead salt with sulphuretted hydrogen and removing excess sulphuretted hydrogen with carbon dioxide (V.Forcher[48]).

(d) By the Drechsel[28] method.

The filtered solutions must be evaporated in vacuo over concen-trated sulphuric acid, in order that crystallisation takes place.

Thus there are various ways of producing metatungstic acid but as regard the preparation of the substituted heteropoly acids, the most significant observations are those of Margueritte,[41] who showed that the addition of mineral acid to less acid tungstates gives rise to metatungstates; and V.Knorre[44] who showed that simply by heating paratungstate solution metatungstate is produced.

Since metatungstic acid and the metatungstates are iso-morphous with the 12-heteropoly tungstates and their salts, it is clear that no separation can be obtained by fractional crystallisation, and that formation of metatungstic acid will give rise to serious difficulties, in purification. The relative stabilities of meta-tungstic acid and the 12-heteropoly acids are, however, very

different, and it is possible that the absence of any reference to this difficulty in the literature is due to decomposition of any metatungstic acid formed in the course of extraction and purification of the more stable 12-heteropoly tungstic acids.

Salts of 12-tungstosilicic acid.

Sodium Salt. $4Na_2O.SiO_2.12WO_3.7H_2O$. or $Na_8\left[Si(W_2O_7)_6\right].7H_2O$.

This 8-basic salt of 12-tungstosilicic acid is reported by Wyrouboff[49]. According to Marignac[50], it is easily formed by boiling an aqueous solution of sodium paratungstate with gelatinous silicic acid. Fine needles of the salt come out of the syrupy solution, but these enclose too much mother liquor to be analysed accurately.

Potassium Salts. $4K_2O.SiO_2.12WO_3.14H_2O$. or $K_8\left[Si(W_2O_7)_6\right].14H_2O$.

The 8-basic salt of the 12-tungstosilicic acid was reported by Marignac[51]. On the basis of more recent work, this salt has been shown to be the salt of the 10-acid (Rosenheim and Jaenicke[53], Kehrmann and Flürscheim[52]).

North and Beal[59], however, specify an 8-basic salt of the 12-acid.

Two other salts $2K_2O.SiO_2.12WO_3.18H_2O$ or $K_4H_4\left[(Si(W_2O_7)_6\right].16H_2O$. and $2K_2O.SiO_2.12WO_3.15H_2O$ or $K_4H_4\left[Si(W_2O_7)_6\right].13\ H_2O$ have also been reported[51,60].

Ammonium Salt.

North and Beal[59] specify an 8-basic salt of the 12-acid.

Guanidine Salts.

Two guanidine salts were reported by Haeberle[25], which he prepared from the free acid by neutralising with different quantities of guanidine carbonate. These are: $4(CN_3H_6)_2O.SiO_2.12WO_3.6H_2O$. or $(CN_3H_6)_8\left[Si(W_2O_7)_6\right]6H_2O$. and $2(CN_3H_6)_2O.SiO_2.12WO_3.12H_2O$. or $(CN_3H_6)_4H_4\left[Si(W_2O_7)_6\right].10H_2O$.

Salts of 10-tungstosilicic acid.

Sodium Salt. There is no sodium salt.

Potassium Salts.

The salt of formula $4K_2O.SiO_2.10WO_3.17H_2O$. or $K_8\left[SiO(W_2O_7)_5\right].17H_2O$. was prepared from a solution of 10-tungstosilicic acid and potassium carbonate in the proportions of 1:4; and of formula $2K_2O.SiO_2 10WO_3.10H_2O$ or $K_4H_4\left[SiO(W_2O_7)_5\right].8H_2O$ when the proportions used were 1:2. [6, 6, 53, 54].

Ammonium Salts.

$4(NH_4)_2O.SiO_2.10WO_3.8H_2O$ or $(NH_4)_8\left[Si(W_2O_7)_5O\right].8H_2O$.

This salt can be prepared by boiling a solution of ammonium paratungstate with gelatinous silicic acid. Addition of ammonia in small quantities causes it to crystallise in small striated prisms. (Marignac)[55]. Copaux[56] claims to have prepared it as a fission product by treating 12-tungstosilicic acid with excess ammonia.

$7(NH_4)_2O.\ 2(SiO_2.10WO_3).25H_2O$ or $(NH_4)_7H\left[SiO(W_2O_7)_5\right].12H_2O$,

the salt which Marignac[51] described as the 8-basic salt of the 12-acid, is prepared by treating 12-tungstosilicic acid with ammonia or by prolonged boiling of the product of addition to the 12-acid of ammonium carbonate, when silica is shed and the salt of the 10-acid results[55]. Marignac[51] also describes a salt of formula

$3(NH_4)_2O.SiO_2.10WO_3.10H_2O$. or $(NH_4)_6H_2[SiO(W_2O_7)_5].9H_2O$.

According to Kehrmann and Flürscheim[57] salts of the type $7R_2O.2(SiO_2.10WO_3)xH_2O$ are formed by addition of alkali carbonates to the corresponding 4-basic salts of 12-tungstosilicic acid. The salts of 10-tungstosilicic acid are in every case poorly characterised when obtained by neutralisation of the free acid. The 7-basic potassium and guanidine salts prepared by the hydrolyses of the 4-basic salts of 12-tungstosilicic acid with the corresponding alkali carbonates are well-defined, however, and gave analyses in agreement with those of the salts directly prepared from the free acid.

Guanidine Salts.

The following salts have been prepared and described by Haeberle.[25]

$7(CN_3H_6)_2O.2(SiO_2.10WO_3).H_2O$. or $(CN_3H_6)_7H[Si(W_2O_7)_5]O$. and

$3(CN_3H_6)_2O.2(SiO_2.10WO_3).11H_2O$ or $(CN_3H_6)_3H_5[SiO(W_2O_7)_5].3H_2O$.

Barium Salt. $4BaO.SiO_2.10WO_3.22H_2O$ or $Ba_4[SiO(W_2O_7)_5]22H_2O$.

This salt crystallises or $Ba_4[SiO(W_2O_7)_5]22H_2O$. of the free acid is saturated with barium chloride. A viscous mass, it dries to a glass. (C.Marignac).[58]

From the literature there emerge three standard methods for preparation of alkali tungstosilicicates, these serving as a source of the free acids, and by double decomposition, as a source of salts other than those of the alkali metals.

1. Boiling of an alkali paratungstate solution with gelatinous

silicic acid, with or without addition of mineral acid. [27] (The solution becomes alkaline during the reaction).

2. Acidification of a mixture of alkali tungstate (or paratungstate) and alkali silicate with mineral acid, at boiling temperature. [32, 62]

3. Saturation of alkali tungstate solutions with alkali fluosilicates until a filtered sample gives no precipitate of hydrated tungstic oxide on addition of mineral acid and boiling. [62] In this case the hydrated silicic acid is obviously derived from the alkali fluosilicate by hydrolysis in the alkali tungstate solution,

$$R_2SiF_6 + 4H_2O = 2RF + 4HF + Si(OH)_4.$$

Since there are no soluble alkali titanates, the second method above cannot be used in the case of titanium.

Separation ofthe free acid from solution was accom-plished by shaking the sodium salt with ether and strong sulphuric acid when the mixture separated into three layers (Drechsel). [28]

1. An ether-water layer (uppermost)

2. An acid-aqueous layer (middle)

3. An "oily" layer of ether-addition-compound of the heter-opoly acid (bottom),

Further purification of the acid was carried out by dissolving the "ether-oil" in absolute alcohol and "reprecipitating" from the alcohol with dry ether.

Analyses.

1. Some 50-60 drops of the "ether-oil" were heated with caustic soda in aqueous solution in order to precipitate the titanium as hydrated titanic oxide (Schoeller). The filtered $TiO_2.xH_2O$ was dissolved in dilute hydrochloric acid, reprecipitated with ammonia and ignited to the oxide TiO_2 in a platinum crucible. The filtrate containing the tungsten as alkali tungstate was made up to a known volume (250 ml) with distilled water and 25 ml portions used to determine the tungsten as cinchonine tungstate. The cinchonine tungstate was decomposed by gentle heat to WO_3, which was weighed.

This method can be used when other non-volatile radicles are present e.g. in analysis of sodium and potassium salts. In the case of the free acid, a quicker and equally accurate method was used.

2. 50-60 drops of the "ether-oil" are placed in a weighed platinum crucible and heated slowly to remove ether and then to a low red heat for twenty minutes. The crucible is cooled and weighed. This is repeated till the weight is constant and gives the weight of a mixture of TiO_2 and WO_3. The mixed oxides are then fused with sodium carbonate, the melt extract-ed with hot water and the precipitated hydrated titanic oxide filtered, washed, redissolved in dilute hydrochloric acid, reprecipitated with ammonia (added till solution is just yellow to methyl orange) and ignited to TiO_2. The weight of tungstic oxide is got by substraction. Thus the ratio TiO_2: WO_3 is found.

PRACTICAL DETAILS of the PREPARATIONS.

On the basis that the product anticipated contains one molecule titanic oxide to twelve molecules of tungstic oxide, 25 grams of normal sodium tungstate should react with 1.71 grams of potassium titanium fluoride, if the reaction is quantitative. Method -3- on page 15, was used in an attempt to prepare alkali tungstotitanates.

1. When 5 grams potassium titanium fluoride, dissolved in boiling water were added to fifty grams of normal sodium tungstate in boiling aqueous solution, made just acid to litmus with dilute hydrochloric acid, i.e. paratungstate in solution, and the mixture boiled for some time, after which a sample was tested with concentrated hydrochloric acid, precipitation of tungstic acid took place. The mixture was thus not stable, and could not be extracted with ether and sulphuric acid.

A white precipitate had been thrown down, presumably titanium oxyfluoride, product of hydrolysis of potassium tit--anium fluoride, so that sufficient titanium had not been left in solution to form the complex compound.

2. To 25 grams normal sodium tungstate in 100 ml boiling water, a solution of 5 grams of potassium titanium fluoride in boiling water was added in six or seven portions. The mixture was kept stirred and the additions took place every two or three minutes. The solution was definitely alkaline at first, and as the solution of potassium titanium fluoride was added became less alkaline. When all was added, the solution was not yet

stable to strong acidification, so small quantities of dilute sulphuric acid were added with constant stirring. A stage was reached at which the colourless reaction mixture changed to clear yellow and no tungstic oxide was precipit--ated by addition of concentrated acid. The solution was cooled to room temperature and about 50 ml ether and one half of the total volume of concentrated hydrochloric acid were added, the whole being kept vigourously stirred through--out. To finish the acidification small quantities of sul--phuric acid were added, about 10 ml in all, and the mixture was allowed to settle. A heavy yellow oil fell to the bottom of the vessel. It was separated, and purified and on anal--ysis gave these figures:

Weight of TiO_2 = 0.0474 gram

" " " WO_3 = 1.9280 "

$$\frac{TiO_2}{WO_3} = \frac{0.0474 \times 232}{1.9280 \times 80} = \frac{1}{14.09}$$

3. To 50 grams normal sodium tungstate in 450 ml water, made just acid to litmus with dilute hydrochloric acid, 10 grams potassium titanium fluoride dissolved in boiling water were gradually added with mechanical stirring. The mixture was allowed to stand for half an hour on the water bath and was then stable to concentrated acid. Extraction, purification, and analysis were carried out as usual.

Weight of $TiO_2 + WO_3$ = 0.2386 grams

" " TiO_2 = 0.0045 "

∴ Weight of WO_3 = 0.2341 grams. $TiO_2 : WO_3 :: 1 : 18.00$.

4. 100 ml boiling water with 10 grams normal sodium tungstate and 8 ml 6N hydrochloric acid were kept boiling and mechanically stirred. The solution was a trifle cloudy. 2 grams potassium titanium fluoride in boiling aqueous saturated solution were added at ten min-ute intervals in 5-10 ml lots. Total volume after all the additions was about 200ml. After standing on a waterbath for about two and a hâf hours the solution was stable. Extracted, purified, and analysed as usual.

Weight of mixed oxides = 1.0660 grams

" " TiO_2 = 0.0190 "

" " WO_3 = 1.0470 "

$$\frac{TiO_2}{WO_3} = \frac{0.0190 \times 232}{1.0470 \times 80} = \frac{1}{19.00}$$

These ether addition compounds, which are obviously not 12-tungstotitanic acid nor 10-tungstotitanic acid, but apparently contain metatungstic acid as well, have the following characteristic properties:

i. The yellowish orange solution in ether gradually deposits tungstic acid and becomes greenish blue and finally deep blue on exposure to light.

ii. When allowed to evaporate spontaniously, the ether-oil becomes a glass-like solid, soluble in water, alcohol, and ether.

iii. The aqueous solution when treated

a. with acid and warmed, precipitates a yellow microcrystalline compound which contains titanium and tungsten.

b. with alkali and warmed, decomposes, giving a transient blue colour, with precipitation oftitanic oxide.

iiii. The solution in alcohol changes from orange to deep blue in sunlight and back to orange in the dark. The alcoholic solution is otherwise perfectly stable.

iiiii. The aqueous solution is not indefinitely stable but gradually deposits a pale yellow amorphous substance.

Attempt to Remove Metatungstic Acid.

The ether oil prepared by methods previously described contained on an average, TiO_2 and WO_3 in a ratio of 1:20. Presumably, metatungstic acid is present (Margueritte[41] and Knorre[44]), and since the Drechsel[28] method of extraction excludes tungstic acid in any other form.

During attempts to prepare the ammonium salt of 12-tungstotitanic acid by saturation of the aqueous solution of the acid with ammonium chloride, a white crystalline precipitate was obtained, almost free from titanium. Since ammonium para-tungstate is the least soluble of the ammonium tungstates, it appeared probable that ammonium paratungstate was being formed from the metatungstic acid present, or by secondary reaction from the tungstotitanic acid. By analogy with the tungsto-silicates, 12-tungstotitanic acid should give rise to the ammonium salt of 10-tungstotitanic acid, the surplus tungstic

oxide forming one or other of the ammonium tungstates. Thus, ammonium chloride was added to an aqueous solution of the ether-oil containing TiO_2 : WO_3 :: 1:20 in the hope that ammonium paratungstate would be precipitated, and that as a result the metatungstic acid would be removed. A white amorphous precipitate came down, was filtered off, and the filtrate was extracted with ether and sulphuric acid. A purified specimen of ether-oil gave these figures on analysis:

1.1171 gram of the mixed oxides gave 0.0055 gram TiO_2 which corresponds to TiO_2 : WO_3 :: 1:68.10.

The result of this treatment is to increase, not decrease, the proportion of tungsten in the ether-oil. If the re-action is as follows:

$$3\,(WO_3)\,.9H_2O + 10NH_4Cl = 10HCl + 5(NH_4)_2O.12WO_3.22H_2O.$$

(metatungstic acid; ammonium paratungstate)

then the hydrogen ion concentration is greatly increased by addition of ammonium chloride. As a result of the disturbed balance, added complications may arise, so ammonium acetate was used in an attempt to precipitate ammonium paratungstate. Results were very similar in this case.

If when ammonium chloride is added to a metatungstate solution, there is no change in hydrogen ion concentration, the white precipitate which results is ammonium metatungstate; if the hydrogen ion concentration increases, then the white precipitate is ammonium paratungstate.

(a) $3H_2O.12WO_3.a.q. + 10NH_4Cl = 3(NH_4)_2O.12WO_3 + 6HCl$

(b) $3H_2O.12WO_3.a.q. + 10NH_4Cl + 2H_2O = 5(NH_4)_2O.12WO_3 + 10HCl.$ [41]

3 ml metatungstic acid ether-oil were made up to 50 ml with distilledwater, and 10 ml portions were titrated with standard baryta solution, using methyl orange as indic-ator.

10 ml metatungstic acid solution ≡ 9.95 ml baryta.

10 ml saturated ammonium chloride solution (blank) ≡ 0.00 ml "

10 ml metatungstic acid solution
10 ml ammonium cloride solution
(precipitated filtered off) ≡ 9.75 ml "

Thus ammonium metatungstate is precipitated, and it is more soluble than the ammonium salt of the heteropoly acid. Thus this method cannot be used to remove the metatungstic acid.

Although, according to Malaprade,[24] metatungstic acid does not react at all with silicic acid to form tungstosilicic acid, an attempt was made to dissolve freshly precipitated gelatinous titanic acid in metatungstic acid. The first attempt was apparently successful, the resulting ether-oil containing $TiO_2:WO_3$ :: 1 : 120. The metatungstic acid had been prepared by slow acidification of sodium paratungstate with dilute mineral acid and extracted with ether and hydrochloric acid. When extracted with sulphuric acid, the metatungstic acid did not dissolve any titanic acid; the apparent solubility had been due to solution of titanic acid in extracted hydrochloric acid, which is ether-soluble. It has since been found that sodium metatungstate slowly dissolves gelatinous titanic acid to form the heteropoly salt.

Since it appeared impossible to remove metatungstic acid, conditions had to be altered to reduce its formation to a minimum.

Attempts to Eliminate Metatungstic Acid Formation.

Addition of mineral acid to alkali paratungstates produces metetungstates (Marguerette)[41]; therefore, acetic acid was tried as a stabilizing agent.

The preparation was carried out exactly as previously, except that 6N acetic acid was used instead of 6N hydrochloric acid to prepare sodium paratungstate from the normal sodium tungstate. Analysis of the extracted ether-oil shows:

0.2643 gram mixed oxides contain 0.0044 gram TiO_2

i.e. TiO_2 : WO_3 :: 1: 20.39

Thus the use of an organic acid in place of a mineral acid does not suppress metatungstate formation.

It was noticed that when the extraction mixture was left to stand, a yellow microcrystalline material, very similar in appearance to tungstic oxide, came out of the acid-aqueous layer. This material was found to contain an appreciable quantity of titanium. Several specimens were collected from different extractions, analyses of which will be recorded later.

By heating an aqueous solution of the ether-oil with a little concentrated hydrochloric acid, a similar, but not identical, yellow material was produced. In order that a specimen of this yellow crystalline material might be obtained, a sample of extracted acid was prepared in the following way:

100 ml water containing 10 grams normal sodium tungstate and 8 ml 6N hydrochloric acid, was kept boiling and stirred mechanically. A saturated solution of 2 grams potassium titanium fluoride in boiling water was added, 5 ml at ten minute intervals to the above solution. The sol--ution was heated on a water bath for two and a half hours and then left to stand over-night. When tested it was stable to concentrated acid, and was extracted with ether and 12 normal sulphuric acid in the usual way.

After purification a sample was analysed:

1.3024 grams of the mixed oxides contain 0.0327 gram TiO_2

i.e. TiO_2 : WO_3 :: 1: 13.40.

After repurification:

0.9163 grams of the mixed oxides contain 0.0247 gram TiO_2

i.e. TiO_2 : WO_3 :: 1: 12.50.

Thus, an acid had been prepared whose composition was closely similar to that of 12-tungstosilicic acid.

The above preparation was repeated following as closely as possible the same conditions.

Analysis showed:

1.0660 grams mixed oxides contain 0.0190 grams TiO_2

i.e. TiO_2 : WO_3 :: 1: 18.83

Attempts were therefore made to standardise the conditions of preparation and extraction.

Preparation.

In order that the titanic oxide, prepared by hydrolysis of the potassium titanium fluoride, may combine with the alkali paratungstate to give the heteropoly salt, the potassium titanium

fluoride must be hydrolysed slowly enough so that the titanium is not lost from solution as the insoluble oxyfluoride. So it was added slowly in dilute solution to a total volume of not less than 350 ml solution for 25 grams normal sodium tungstate. The stable mixture was extracted and a sample analysed:

0.6068 gram mixed oxides contain 0.0078 gram TiO_2

i.e. $TiO_2 : WO_3 :: 1 : 26.48$.

On addition of the 12-normal sulphuric acid during extraction, the whole solution was heated slightly, and decomposition may have taken place in the strongly acid solution.

Extraction.

In order to prevent this, the extraction was carried out as follows:

The beaker containing the stable solution was immersed in a freezing mixture and an equal volume of dry ether added. The liquids were stirred with a mechanical stirrer while again an equal volume of 12N sulphuric acid was added gradually from a dropping funnel. After extraction the ether-oil was allowed to settle and separated off. Purified and analysed, the following figures were obtained.

1.0354 gram mixed oxides contain 0.0316 gram TiO_2

i.e. $TiO_2 : WO_3 :: 1 : 10.96$.

Analyses of specimens, prepared and extracted as described, are as follows:

(1) 0.8186 gram mixed oxides contain 0.0195 gram TiO_2

i.e. $TiO_2 : WO_3 :: 1 : 14.10$

(2) 0.8798 gram mixed oxides contain 0.0200 gram TiO_2

i.e. $TiO_2 : WO_3 :: 1 : 14.80$

(3) 0.9208 gram mixed oxides contain 0.0248 gram TiO_2

i.e. TiO_2 : WO_3 :: 1: 12.46

(4) 1.3320 gram mixed oxides contain 0.0375 gram TiO_2

i.e. TiO_2 : WO_3 :: 1: 12.05

Thus, by adjusting conditions of preparation and extraction, samples of an acid corresponding to 12-tungstotitanic acid can be obtained. An occasional preparation gives a sample low in titanic oxide. For example, a preparation was carried out without careful adjustment of the normal sodium tungstate to sodium paratungstate. The ether-oil on analyses gave 0.0108 gram TiO_2 from 0.7934 gram of the mixed oxides, i.e. TiO_2 :WO_3: :1:25.10.

None of the samples of the ether-oil crystallised on evaporation but simply dried to a glass, it is not definite whether this is the 12-tungstotitanic acid or a mixture of metatungstic acid and 10-tungstotitanic acid. Until samples are prepared containing titanic oxide and tungstic oxide in the ratio 1:10, this may be written as $TiO_2 . 12WO_3 \; xH_2O$, analgous to 12-tungstosilicic acid.

<u>The Yellow Microcrystalline Material.</u>

Several samples of the yellow material, referred to earlier, which is formed in the acid-aqueous layer in the extractions were obtained by filtering off, washing till free from acid and drying in air. These samples were taken from the later extractions where the extracted ether-oil contained TiO_2 :WO_3 in the approximate ratio of 1:12.

First Sample, pale yellow microcrystalline powder

Weight of original material = 1.0134 grams

Ignition loss (low red heat) 0.1600 grams

Weight of mixed oxides 0.8534 grams

Weight of TiO_2 0.0300 grams

Weight of WO_3 0.8234 grams

TiO_2 : WO_3 :: 1: 9.48

empirical formula: $TiO_2 . 9.48\ WO_3 . 24H_2O$. or $H_8\left[TiO(W_2O_7)_5\right] . 20H_2O$

Second Sample, same appearance.

Weight of original material 0.9530 grams

Ignition Loss 0.1816 grams

Mixed Oxides 0.7764 grams

Weight of TiO_2 0.0287 grams

Weight of WO_3 0.7427 grams

TiO_2 : WO_3 :: 1: 9.61

empirical formula: $TiO_2 . 9.61 WO_3 . 28H_2O$. or $H_8\left[TiO(W_2O_7)_5\right] . 24H_2O$.

Although those two analyses would point to this material as being the 10-acid, the water of crystallisation is different and as will be shown, it is very doubtful if it is. Various other samples of this yellow material have occurred which contain TiO_2 : WO_3 :: 1:6.85; 1:9.20; 1:15.63. It was found that the greater proportion of titanic oxide in the extracted acid, the greater proportion of titanic oxide in the yellow material. Apparently, then, this material formed in the separating funnel is a mixture of decomposition products. Also, when a sample of this yellow material containing TiO_2 : WO_3 :: 1:9.73 is boiled with dilute hydrochloric acid it loses titanic oxide giving a material having TiO_2 : WO_3 :: 1:27.20.

Yellow Microcrystalline Material prepared by heating the ether-oil with hydrochloric acid.

By heating the extracted ether-oil, containing $TiO_2:WO_3::1:12$ approximately, with distilled water containing some concen--trated hydrochloric acid on the water-bath for from two to three days, a deep yellow crystalline material is formed. It is different in appearance from the above yellow materials. Unfortunately, a small quantity only can be obtained. Analyses of two samples are as follows:

(1) Weight of air dried material 0.3097 gram.

Loss on gentle ignition 0.0289 gram.

Weight of mixed oxides 0.2808 gram.

Weight of TiO_2 0.0096 gram.

Empirical formula $10.8H_2O.TiO_2.9.73WO_3$. or

$$H_8\left[TiO(W_2O_7)_5(H_2O)_6\right].$$

(2) Weight of air dried material 0.2995 gram.

Loss on gentle ignition 0.0495 gram.

Weight of mixed oxides 0.2500 gram.

Weight of TiO_2 0.0090 gram.

Empirical formula: $TiO_2.9.6WO_3.24.34H_2O$ or

$$H_8\left[TiO(W_2O_7)_5\right].20H_2O.$$

Since these compounds are more definitely crystalline and are stable to heating with hydrochloric acid, it may be that they are two different hydrates of 10-tungstotitanic acid.

Properties.

The acid is not soluble in water. With dilute acid, hot or cold, it is unchanged. Caustic alkali decomposes it immediately, precipitating hydrated titanic acid. It is insoluble in alcohol and in ether.

Direct Preparation of 10-tungstotitanic acid.

From Margueritte's observations[47], which have been repeatedly confirmed in this work, addition of acid to alakli paratungstate, especially in hot solution, gives rise quantitive--ly to alkali metatungstate. If the saturating agent is already acid by hydrolysis, metatungstate formation will inevitably precede absorption of titanic acid by the paratungstate to give alkali tungstotitanate.

A one per cent solution of potassium titanium fluoride has, at room temperature, a p_H of about 3.5 and is thus distinctly acid. Since it is used simply as a source of titanic acid, being hydrolysed by the more alkaline paratungstate solution; in order to give quantitative saturation, the titanic acid must be taken up by the paratungstate at the same rate as the hydrofluoric acid is set free by the hydrolysis of the potassium titanium fluoride. If this is not the case, without doubt metatungstate will be formed.

It was discovered that sodium titanium fluordie, when prepared from titanic oxide and hydrofluoric acid, in equivalent quantities, and addition of the requisite amount of sodium fluoride, was a crystalline salt analysing in accordance with the formula Na_2TiF_6. Its aqueous solution was neutral, so here was a possible saturating agent which would not acidify paratungstate to metatungstate.

Method of Preparation.

25 grams of normal sodium tungstate were dissolved in 400 ml water and the pH adjusted to 6.4 (paratungstate) with nitric acid. 3 grams solid titanium fluoride were added to the boiling mechanically stirred sodium paratungstate solution, where

it dissolved almost immediately to a clear colourless solution. This was allowed to boil and kept stirred for two hours, when it was stable to extraction and the p_H had fallen to 5.4. It was found that if the extraction were postponed till the following day, the ether-oil separated more quickly and completely. After purification, analysis showed:

0.9588 gram mixed oxides contain 0.0335 gram TiO_2

i.e. TiO_2 : WO_3:: 1: 9.55.

Many other preparations were carried out in this way, and all of them gave an ether-oil containing TiO_2 : WO_3 in the region of 1:10.

Other analyses figures are:

TiO_2 : WO_3::1:10.60; TiO_2: WO_3::1:10.50; TiO_2: WO_3::1:10.45;

TiO_2 : WO_3::1:10.60; TiO_2: WO_3::1:10.67.

The sooner the ether-oil is separated the higher is the TiO_2 :WO_3 ratio. Second and third fractions of ether-oil contain progress--ively less titanic oxide, and obviously in strongly acid solu--tion the balance is disturbed with consequent generation of meta-tungstic acid.

When in the above preparation the sodium titanium fluoride is added in solution instead of in the solid state, the TiO_2 : WO_3 ratio is lower e.g. 1:11.60; 1: 12.50. Here, where the sodium titanium fluoride is added more slowly there is more time for transformation ofparatungstate to metatungstate on heating (Knorre)[44].

The ether-oil from a specimen was dissolved in alcohol and allowed to crystallise in air. At first a syrupy liquid appeared which became a clear yellow glass. When ground up in

a mortar, it closely resembled the yellow crystalline material prepared by treatment of the ether oil with hydrochloric acid.

Analysis.

2.5924 grams were heated at 110° till constant weight.

Loss at 110°	0.2328 gram.
Loss at 125°	0.0000 gram.
Loss on gentle ignition (low red heat)	0.1550 gram.
Weight of TiO_2	0.0688 gram.
Weight of WO_3	2.1358 gram.

Empirical formula: $10H_2O.TiO_2.10WO_3.15H_2O$. or $H_8\left[TiO(W_2O_7)_5.(H_2O)_6\right].15H_2O$

Properties.

This yellow material is insoluble in water, acids, ether, and alcohol. It is decomposed by caustic alkali and ammonia, precipitating titanic acid.

SALTS OF TUNGSTOTITANIC ACID.

Sodium Salt.

A stable solution from a sodium titanium floride preparation was crystallised, filtered and crystallised again. Eventually well-formed crystals appeared, which contained sodium, tungsten and titanium. The ratio TiO_2 : WO_3 was 1: 8.90 and the substance was probably the sodium salt of the 10-acid, con-taminated with a little sodium titanium fluoride. The salt is very soluble and thus extremely difficult to obtain pure.

Potassium salt.

The potassium salt of the 10-acid probably exists in

solution when potassium titanium fluoride is used to saturate potassium paratungstate solution, or even when it is used to saturate sodium paratungstate solution. But again it has not been found possible to obtain a specimen pure enough for analysis. When specimens of the free acid are treated with alkali carbonate they are decomposed, so it has not been possible to prepare the alkali salts by direct neutralisation of the 10-acid.

Ammonium Salt.

When a concentrated solution of sodium tungstotitanate, as it had been prepared from sodium paratungstate by saturation with potassium titanium fluoride, was acidified with a little dilute hydrochloric acid and treated with a saturated solution of ammonium chloride, a brownish-white precipitate came down which was washed and analysed:

1. Weight of air-dried salt 0.5416 gram.
   Loss on gentle ignition 0.0724 gram.
   Weight of TiO_2 0.0158 gram.
   Weight of WO_3 0.4534 gram.
   Percentage of ammonia 3.66%

Empirical formula: $3(NH_4)_2O.TiO_2.10WO_3.15H_2O$ or

$$(NH_4)_6H_2\left[TiO(W_2O_7)_5\right].14H_2O$$

2. A second specimen was prepared in the same way.
   Weight of air dried salt 0.4754 gram.
   Loss on gentle ignition 0.0982 gram.
   Weight of TiO_2 0.0131 gram.
   Weight of WO_3 0.3461 gram.
   Percentage of ammonia 3.81%

Empirical formula: $3(NH_4)_2O.TiO_2.10WO_3.43.5H_2O$ or

$(NH_4)_6\,H_2[TiO(W_2O_7)_5].42.5H_2O$.

These salts were both prepared from solutions from which ether-oils were extracted containing $TiO_2:WO_3$ in the ratio of 1:12 approximately, which would point to there being no ammonium salt of the 12-acid, if there is indeed a 12-acid.

Guanidine Salts.

It was found in the earlier preparations of the heteropoly acid, that guanidine hydrochloride precipitated heteropoly and isopoly acids together from the solution, as insoluble guanidine salts. These salts are amorphous and cannot be separated by recrystallisation from water.

Reagent:

50 grams guanidine carbonate were neutralised to methyl orange with hydrochloric acid and made up to 250 ml with distilled water. This gives an almost saturated solution.

An aqueous solution containing an ether oil of composition $TiO_2:WO_3$ :: 1:25.10 was treated with guanidine hydrochloride solution. The white amorphous precipitate was washed with dilute guanidine hydrochloride solution, drained, dried and analysed. 0.7604 gram of the salts contain0.0088 gram TiO_2 and 0.6166 gram WO_3. i.e. $TiO_2:WO_3$ :: 1:24.16.

Guanidine salts were prepared from ether oils containing $TiO_2:WO_3$ in the ratio 1:12.88 (A) and 1:12.00 (B), in the following way:

About 5 ml of the ether oil was dissolved in distilled water and the ether driven off by a current of air. 20-25 ml. guanidine hydrochloride solution were added to the aqueous solution

and caused immediate precipitation of white amorphous salts. These were washed with dilute guanidine hydrochloride solution, drained, air-dried and analysed.

(a) 0.5076 gram of the salt contain 0.0110 gram of TiO_2 and 0.4188 gram of WO_3. Guanidine was estimated by means of the Kjeldahl method.

Loss on ignition	16.70%
Titanic oxide	2.17%
Tungstic oxide	81.09%
Guanidine oxide	12.83%
Water	3.81%

Empirical formula: $3.5(CN_3H_6)_2O.TiO_2.12.9WO_3.8H_2O$ or

$$(CN_3H_6)_7H\left[TiO(W_2O_7)_5\right].7.5H_2O.$$

(b) 0.2636 gram of salt contain 0.0063 gram TiO_2 and 0.2174 gram WO_3.

Loss on ignition	16.71%
Titanic oxide	2.39%
Tungstic oxide	80.34%
Guanidine oxide	10.90%
Water	5.80%

Empirical formula: $3(CN_3H_6)_2O.TiO_2.12WO_3.12H_2O$ or

$$(CN_3H_6)_6H_2\left[TiO(W_2O_7)_5\right].11H_2O.$$

It is possible, but improbable, that these salts are derivatives of 12-tungstotitanic acid. It is much more probable that they are mixtures of guanidine metatungstate and guanidine 10-tungstotitanate.

A guanidine salt of the 10-acid has not so far been prepared, although it could be done directly by precipitation from an aqueous solution of the ether-oil of 10-tungstotitanic acid.

Barium salt.

It was found that when barium chloride solution was added to a balanced mixture from a saturation with pot--assium titanium fluoride (extracted ether-oil contained TiO_2 : WO_3 :: 1 : 12 approx.) a white precipitate containing a very small percentage of TiO_2 was obtained. Barium meta--tungstate cannot be prepared pure by addition of barium chloride to alkali metatungstate solution except in hot dilute solution and in presence of a little mineral acid. In cold concentrated solution a large proportion of the tungsten is precipitated as the very slightly soluble barium tritungstate $BaO.3WO_3.6H_2O$, a hydrolysis product of barium metatungstate. Precipitation with concentrated barium chloride solution at room temperature thus serves to remove a substantial amount of unwanted alkali metatungstate.

It was found, however, that the barium tungstotit--anate could not be obtained in sufficient quantity by this method.

When barium chloride solution was added to a balanced mixture from a saturation with potassium titanium fluoride, which had been adjusted to paratungstate with sulphuric acid, a heavy white precipitate of barium sulphate, barium fluoride and barium tritungstate was formed. This was filtered off and the filtrate left to crystallise. Since there was a possibil--ity that the barium tungstotitanate had been co-precipitated with the previous precipitate, it was boiled with water and the filtrate was set aside to crystallise. A beautiful white crystalline salt came out of this solution, but no crystallis-

-ation took place from the first filtrate. The salt, which was very heavy, was filtered off, washed with a little water, air-dried and analysed.

Method of analysis:

About 1.2 grams of the salt was dried at 110° and then ignited gently. The residue was fused with sodium carbon--ate, the melt extracted with water, and the residue of barium carbonate and titanic oxide washed with sodium carbonate solu--tion. This residue was then washed with cold dilute hydro--chloric acid, then hot hydrochloric acid giving a solution containing the barium and most of the titanium as chlorides. The filter paper retained a little titanic oxide and tungstic oxide. It was dried and ignited, and the sodium carbonate fusion repeated. The filtrate was added to the main tungsten extract, and the filter paper was washed with hot dilute hydrochloric acid and water, the washings being added to the main barium-titanium extract. The precipitated titanic oxide was filtered through this paper. The barium was precipitated in the hydrochloric acid solution with dilute sulphuric acid and the titanium with ammonia from the fil--trates of the barium. The tungsten was precipitated with cin--chonine hydrochloride and gently ignited to tungstic oxide. (When the precipitate of titanic oxide was coloured it was fused again with sodium carbonate, redissolved and reprecipitated with ammonia). Analyses of two samples are as follows:

	A	B
Weight of air-dried salt	1.1044 gr.	1.4087 gr.
Loss in weight at 110°	0.1064 gr.	0.1354 gr.
Loss on gentle ignition	0.0416 gr.	0.0534 gr.
Weight of BaO	0.1498 gr.	0.1927 gr.

Weight of TiO_2	0.0268 gr.	0.0334 gr.
Weight of WO_3	0.7424 gr.	0.9739 gr.
Total weight	1.0670 gr.	1.3888 gr.

From these analyses figures (A) has the empirical formula:

$2.9BaO.6.9H_2O.TiO_2.9.54WO_3.17.6H_2O$ or $Ba_3H_2\left[TiO(W_2O_7)_5.(H_2O)_6\right].18H_2O.$

(B) :

$3BaO.7H_2O.TiO_2.10WO_3.18H_2O$ or $Ba_3H_2\left[TiO(W_2O_7)_5.(H_2O)_6\right].18H_2O.$

which shows that the barium salt is the 6-basic 24-hydrate.

Calcium Salt.

There is no reference to a calcium salt of 10-tungstosilicic acid in the literature.

By neutralising an aqueous solution of the ether-oil of 10-tungstotitanic acid to methyl orange with just enough calcium carbonate, filtering off any trace of undissolved carbonate, and heating on a water bath until crystallisation took place the calcium salt of 10-tungstotitanic acid was obtained. This salt is extremely soluble.

Method of analysis:

About two grams of the salt were ignited gently in a platinum crucible and then fused with sodium carbonate. The calcium carbonate and titanic oxide residue was filtered off and dissolved in dilute hydrochloric acid. Titanium was separated from calcium by adding a fresh solution of ammonium sulphide to the diluted solution, when titanic acid was precipitated. This separation was done twice and the calcium was then precipitated as calcium oxalate and ignited to calcium oxide. The tungsten was precipitated as cinchonine tungstate and gently ignited to WO_3.

Analysis:

Weight of air-dried salt	2.1544 gram
Loss on gentle ignition	0.3154 gram
Weight of CaO	0.1295 gram
Weight of TiO_2	0.0564 gram
Weight of WO_3	1.6636 gram
Total Weight.....	2.1649 grams.

(this total weight is 0.0105 gr. too high, probably due to the calcium which tends to run high when estimated in this way).

Empirical formula: $3.28CaO.TiO_2.10.02WO_3.24.89H_2O$ or

$$Ca_3H_2\left[TiO(W_2O_7)_5\right].24H_2O.$$

Thus barium and calcium give identical salts of 10-tungstotitanic acid.

THE MECHANISM OF FORMATION OF TUNGSTOTITANIC ACIDS.

In order that pure samples of 12-tungstotitanic acid (if it exists) and 10-tungstotitanic acid may be prepared, and understanding of the way in which the reaction takes place is necessary.

The source of tungsten is an alkali paratungstate, usually sodium paratungstate. According to H. Th. St. Britton and W.L.German,[73] fairly well-defined "breaks" in the curve drawn from results of potentiometric titrations of sodium tungstate with hydrochloric acid, occur between pH values 6.4 and 6.1, corresponding to the salts $3Na_2O.7WO_3$ and $5Na_2O.12WO_3$. The literature is not clear as to which of these represents sodium paratungste. It has been found that addition of 97.2 ml of normal mineral acid to 25 grams normal sodium tungstate in 400 ml water gives a sol-

-ution with p_H of 6.4. The sodium tungstate in this solution corresponds closely to $3Na_2O.7WO_3$. Addition of a small amount of strong acid or strong base alters the p_H of the solution appreciably, which points to the neighbourhood of an equivalence point.

In later preparations of 12-tungstotitanic acid, the starting solution was prepared as described above, so that the p_H was 6.4 and the salt in solution was $3Na_2O.7WO_3$. If the potassium titanium fluoride were hydrolysed in its entirety to titanic acid and hydrofluoric acid, then the reaction might be represented thus:

(1) $\frac{12}{7}(3Na_2O.7WO_3) + TiO_2 + 4HF = 3Na_2O.TiO_2.12WO_3 + 4NaF + \frac{1}{7}Na_2O$

or

(2) $\frac{12}{7}(3Na_2O.7WO_3) + TiO_2 + 4HF = 4Na_2O.TiO_2.12WO_3 + \frac{16}{7}NaF + \frac{12}{7}HF.$

In equation (1) the reaction shows elimination of free alkali, and as a result the reaction will cease, since presumably the p_H of solutions of heteropoly tungstates should be of the same order as p_H given by equivalent solutions of metatungstates (p_H of 5.8--5.4). In equation (2) free acid is liberated and as a result of its action on sodium paratungstate, metatungstate will be produced in solution. The solution however would be stabilised and this is not the case. The reaction presumably follows equation (1).

$\frac{2}{7}$ equivalent nitric acid was added to a preparation con-taining sodium paratungstate and potassium fluoride in the ratio $1:\frac{12}{7}$. This did not bring about stabilisation. There was a slight white precipitate of titanium oxyfluoride and the p_H of the solution was 6.2. This was repeated on a second preparation and exactly

the same results were obtained. Thus the reaction is not quantitative. The two solutions were mixed and one molecular proportion of potassium titanium fluoride added to the boiling mixture. Then the proportions in solution were

$\frac{12}{7}(3Na_2O.7WO_3) : K_2TiF_6 :: 1:1.5$.

The solution was stable to acidification and the p_H was 5.7.

The extracted acid when purified and analysed gave $TiO_2 : WO_3 :: 1:13.5$ and 1:13.0.

This was repeated and the results confirmed.

Thus the substituted metatungstates exist in the same p_H as the metatungstates, which is what is to be expected,

Preparation of sodium paratungstate.

$$12Na_2WO_4 + 13.5\ HNO_3 = \frac{12}{7}(3Na_2O.7WO_3) + 13.5\ NaNO_3$$

This gives a solution of p_H 6.4.

Preparation of 12-tungstotitanic acid.

Addition of $\frac{3}{2}$ molecular proportion of potassium titanium fluoride to $\frac{12}{7}$ molecular proportion of sodium paratungstate causes stabilisation. This may mean that 12-tungstotitanate is formed.

$$\frac{12}{7}(3Na_2O.7WO_3) + \frac{3}{2}\ K_2TiF_6 + \frac{5}{2}\ H_2O = 4Na_2O.TiO_2.12WO_3 + \frac{1}{2}\ TiOF_2 + \frac{16}{7}NaF + 3KF + \frac{19}{7}HF$$

Although Wyrouboff describes sodium 12-tungstotitanate as the 8-basic salt, the free hydrofluoric acid here would alter the p_H of the solution more than from 6.4 to 5.8-5.4.

A less basic salt may therefore be formed.

$$\frac{12}{7}(3Na_2O.7WO_3) + \frac{3}{2}K_2TiF_6 + \frac{5}{2}\ H_2O = 3Na_2O.TiO_2.12WO_3 + \frac{1}{2}\ TiOF_2 + 3KF + \frac{30}{7}NaF + \frac{5}{7}HF$$

There is still reserve of alkali in the 12-tungstotitanate, but it is unlikely that a less basic salt is formed since the reaction tends to become more acid (p_H changes from 6.4 to 5.7). Addition of a

further small quantity of potassium titanium fluoride causes a gradual decrease in pH to 5.2. Thus probably the salt present in the balanced mixture is represented accurately by the formula $3Na_2O.TiO_2.12WO_3$, or the 6-basic salt.

The ammonium salt isolated from these preparations has analyses figures which correspond with the 6-basic salt, but it is a salt of the 10-acid.

Preparation of 10-tungstotitanic acid.

The saturations with sodium titanium fluoride produce 10-tungstotitanate if the saturating agent is added in the solid state. The starting solution is again sodium paratungstate, $3Na_2O.7WO_3$.

The reaction may be:

(1) $\frac{10}{7}(3Na_2O.7WO_3)+Na_2TiF_6+\frac{5}{7}H_2O = 3Na_2O.TiO_2.10WO_3+\frac{32}{7}NaF+\frac{10}{7}HF$

(1) $\frac{10}{7}(3Na_2O.7WO_3)+Na_2TiF_6+\frac{5}{7}H_2O = 3Na_2O.TiO_2.10WO_3+\frac{32}{7}NaF+\frac{10}{7}HF$

(2) $\frac{10}{7}(3Na_2O.7WO_3)+\frac{3}{2}Na_2TiF_6+\frac{17}{14}H_2O = 4Na_2O.TiO_2.10WO_3+\frac{25}{7}NaF+\frac{17}{7}HF$

(3) $\frac{10}{7}(3Na_2O.7WO_3)+Na_2TiF_6+\frac{12}{7}H_2O = 4Na_2O.TiO_2.10WO_3+\frac{18}{7}NaF+\frac{24}{7}HF$

Again (2) and (3) are exceedingly unlikely, and the reaction in all probability follows most closely equation (1).

On the other hand it may be that salts more acid than the 6-basic are formed, or that the hydrofluoric acid set free during the reaction combines with alkali paratuhgstate to give metatungstate. On this basis, and assuming that the salt formed is $3Na_2O.TiO_2.10WO_3$: $2(3Na_2O.7WO_3)+K_2TiF_6 = 3Na_2O.TiO_2.10WO_3+Na_2O.4WO_3+4NaF+2KF$, this gives three molecules sodium 10-tungstotitanate to one molecule sodium metatungstate. The acid, if both acids are extracted completely, would have

$TiO_2:WO_3::1:14$. For the quantities actually used, $\frac{12}{7}$ sodium paratungstate would require $\frac{6}{7}$ potassium titanium fluoride assuming that this hydrolyses completely to $Ti(OH)_4$, and the latter is quantitatively absorbed by the alkali paratungstate. Experiment shows that stability is not reached below 1.5 molecules potassium titanium fluoride. Since saturation of the paratungstate is complete when there is $TiO_2:WO_3::1:10$, the excess potassium titanium fluoride must, if there is no loss of tungstic oxide from the solution, give rise to titanic acid or titanium oxyfluoride, setting free, hydrofluoric acid, the p_H of the balanced mixture being 5.4-5.8 and thus above the p_H at which hydrolysis of potassium titanium fluoride begins.

Actually however, there is a substantial amount of material containing both titanium and tungsten thrown down during the saturation. Loss of tungsten will raise the proportion of titanium to tungstan in the reaction mixture and thus tend to prevent formation of metatungstate by leaving alkali oxide in solution to take up the hydrofluoric acid set free. In addition the 6-basic sodium salt will u ndoubtedly be capable of taking up a certain amount of hydrofluoric acid to give a more acid salt.

As regards potassium titanium fluoride at least, there will probably be some metatungstate formation, since this gives initially a solution of p_H 3.5 for a one per cent solution. This is presumably not the case with sodium titanium fluoride, which gives a neutral aqueous solution. The composition of the acid pre-pared with potassium titanium fluoride is therefore ambiguous. It may be either $6H_8\left[Ti(W_2O_7)_6\right]$ or $6H_8\left[TiO(W_2O_7)_5\right] + H_{10}\left[H_2(W_2O_7)_6\right]$.

The well-defined 6-basic salt, barium 10-tungstotitanate, can be isolated from mixtures containing TiO_2: WO_3 in any ratio from 1:10 to 1:20, and over. No barium salt of 12-tungsto--titanic acid has been isolated, though this ofcourse does not prove its non-existence.

SUMMARY OF RESULTS.

Free acid.

From analogy with the tungstosilicic acids, only 10-tungstotitanic can be considered definite. The method of pre--paration shows that the apparaent 12-acid is probably a mixture of the 10-acid with metatungstic acid, especially as some of the earlier preparations using potassium titanium fluoride as saturating agent give TiO_2: WO_3 higher than 1:12. Also, com--plexes of Ti^4 with organic acids are usually of the titanyl type containing TiO^2 .

Salts.

The definite salts are the ammonium , barium and calcium salts. These are all 6-basic, the best defined being the barium salt.

Their formulae are:

Ammonium salt.

$$(NH_4)_6H_2\left[TiO(W_2O_7)_5\right].14H_2O.$$

Calcium salt.

$$Ca_3H_2\left[TiO(W_2O_7)_5\right].24H_2O.$$

Barium salt.

$$Ba_3H_2\left[TiO(W_2O_7)_5\right].24H_2O \text{ or } Ba_3H_2\left[TiO(W_2O_7)_5.(H_2O)_6\right].18H_2O$$

From the analytical point of view, the anomalous behaviour

of tungsten in pyrosulphate fusion with titanium can be accounted for by the formation of 10-tungstotitanic acid. Hydrolysis of this in acid solution gives the yellow solid previously described, closely resembling tungstic oxide but containing a definite porportion of titanic oxide.

Use of tannin in place of cinchonine as a precip-itant for tungsten, following on a pyrosulphate fusion, gave according to Schoeller[1] a precipitate containing an appreciable amount of titanic oxide, which was not removed by repeated fusion and precipitation with tannin. There is no doubt that this was due to tannin 10-tungstotitanate.

PART 2.

HETEROPOLY TUNGSTEN-IRON COMPLEXES.

Introduction.

Since the work on tungstotitanic acids arose primarily from an analytical problem, it seemed desirable to investigate the possibility of complexes of tungsten with othere metals associated in analysis with titanium. Iron, since it is closely associated with titanium, and also with tungsten, in ores and minerals, seemed a suitable choice.

A titanium-tungsten complex acid analogous to 10-tungstosilicic acid has been prepared. Derivatives have also been isolated and analysed. These belong to the limit-ing series of heteropoly aompounds, but not to the saturated series, and are formulated $H_8\left[TiO(W_2O_7)_5\right].xH_2O$, according to Rosenheim and Jaenicke.[9]

Attempts were therefore made to prepare iron-tungsten compounds of the above type: $H_9\left[Fe(W_2O_7)_6\right].xH_2O$ and $H_9\left[FeO(W_2O_7)_5\right].xH_2O$.

Historical survey.

Hitherto work had been done on compounds of iron and tungsten by A.Laurent,[63] who fused excess wolfram with pot-assium nitrate and potassium carbonate, and obtained a res-idue partly soluble in boiling water, which deposited on cooling a brown gummy mass. On treatment with hydrochloric acid and evaporation in hot solution, this gave large six-sided prisms with regular faces of the type $W_5O_{18}M_6$. In the cold, the salt was not decomposed by concentrated acids nor was ferric hydroxide precipitated by alkalis. No precipitate

was produced with potassium ferrocyanide, and more remarkable, the ferric iron was not reduced by sulphuretted hydrogen nor ammonium sulphide. On heating with potassium hydroxide or ammonium hydroxide a "ferric tungstate" was slowly precipitated, and acid then precipitated hydrate tungstic oxide in quantity.

The "free acid" was obtained from the potassium salt by decomposition with chloroplatinic acid, the potassium chloroplatinate filtered off, and the filtrate evaporated to a syrupy mass. The "free acid" was not analysed. On ignition the salts were dehydrated and remained as insoluble residues.

Treatment of wolfram with aqua regia and solution of the residue in ammonia, gives in addition to ammonium para--tungstate, a mother liquor, which on neutralisation with hydro--chloric acid forms crystalline needles of a salt containing ferric iron, manganese, tungstic oxide and water. The salt must have a complex form, as none of the free ions are detectable in the undecomposed salt. On boiling with acids or alkalis the metallic oxides are deposited. The ammonium salt when treated with chloroplatinic acid gives the free ferri-mangani-tungstic acid as a syrup.

The brown gummy mass described above, can be boiled with sodium carbonate without precipitation of ferric hydroxide, and must contain an acid of another type than that given by acid treatment.[63] The formulae Laurent attributed to some of his compounds are as follows:

$9K_2O.12H_2O.2Fe_2O_3.45WO_3.54H_2O.$

$18K_2O.3H_2O.2Fe_2O_3.45WO_3.54H_2O.$

$21BaO.2Fe_2O_3 45WO_3.27H_2O.$

According to H.Schwer,[64] and A.Rosenheim and H.Schwer,[65] these compounds were not analytically pure, and the pure compounds could not be formed by the above methods.

The existance of the iron compound of the type $M_2O.xFe_2O_3.yWO_3$ was conjectured by C.N.Balke and E.H.Smith.[66]

In more recent times, work has been done by Rosenheim and Schwer.[67,68] By saturation of sodium paratungstate solutions with ferric chloride solution, added in small amounts, until the first-formed precipitate ceased to redissolve, they obtained an orange-coloured solution, which gave, on treatment with potassium chloride, ammonium chloride and guanidine hydrochloride, sparingly soluble yellow crystalline precipitates. These are formulated:

$4K_2O.Fe_2O_3.12WO_3.aq.$ or $K_4H_5\left[Fe(WO_4)_6\right]aq.$

$4(NH_4)_2O.Fe_2O_3.12WO_3.aq$ or $(NH_4)_4H_5\left[Fe(WO_4)_6\right].aq.$

$4(CN_3H_6)_2O.Fe_2O_3.12WO_3.aq.$ or $(CN_3H_6)_4H_5\left[Fe(WO_4)_6\right]aq.$

The tungstoferric acid they described as a 9-basic acid, and giving 4-basic substituted salts, as shown by conductivity experiments. Because of the instability of the complex anion, there are no higher basic salts.[68]

Constitution.

On the basis of conductivity measurements, the tungstoferrites are regarded as derivatives of the 9-basic acid $H_9\left[Fe(WO_4)_6\right]aq.$ namely tungstoferric acid.[44] This acid may be regarded as a substituted analogue of the hypothetical "paratungstic acid" $H_{10}\left[H_2(WO_4)_6\right]aq.$ According to Rosenheim and Schwer,[44] ferric iron, aluminium and chromium form a number

of compounds with molybdates and also with tungstates containing anions of complex nature. They are, according to the Co-ordina--tion Theory, heteropoly chromites, aluminates and ferrites. Corresponding to the trivalent central atom are the hypothetical 9-basic salts of the type $H_9\left[M^3\ (XO_4)_6\right]$ where M is aluminium, chromium or ferric iron, and X is tungsten or molybdenum; and these compounds are directly related to 12-tungstoboric acid $H_9\left[B(W_2O_7)_6\right]\cdot aq.$

Preparation.

Rosenheim[65] gives no information as to the relative amounts of sodium paratungstate and ferric chloride solution used in his preparations, but speaks merely of "exact saturation" of sodium paratungstate with ferric chloride.

H.Struve[69] claims to have obtained molybdoferrites by boiling alkali trimolybtate with ferric hydroxide. J.G.Gentele[70] has prepared them from solutions of ferric sulphate and of ammonium iron alum and ammonium molybdate. E.Steinacker[71] also prepared the compounds and described them.

F.Parmentier[72] obtained molybdoferrite by heating ferric oxide with potassium molybdate in presence of water in a sealed tube at 150° degrees. His compound was crystalline and of the type:

$$2R_2O.Fe_2O_3.10MoO_3.xH_2O.$$

The potassium and ammonium salts with formulae:

$3K_2O.Fe_2O_3.12MoO_3.$ or $K_3H_6\left[Fe(MoO_4)_6\right].7H_2O.$ and

$3(NH_4)_2O.Fe_2O_3.12MoO_3.$ or $(NH_4)_3H_6\left[Fe(MoO_4)_6\right].7H_2O.$

have been prepared from a saturated solution of sodium paramolybdate and iron alum by treatment with potassium chloride or ammonium

chloride. The potassium salt comes out as colourless crystals with 3 molecules of water of constitution.[75] The ammonium salt crystallises in small white prisms and was prepared by Marckwald.[76]

Further work on these salts was carried out by R.D.Hall[77] and Rosenheim and Schwer.[75]

Isomorphous with these compounds are the corresponding compounds of aluminium, chromium, tri-valent cobalt and rhodium described by Zambonini and Caglioti.[78]

Thus, throughout the literature heteropoly compounds of trivalent iron with tungsten and molybdenum have been salts of the paratungstate type. No free acid either of the substituted metatungstate type or of the substituted paratungstate type has been described,[28] nor does the Drechsel method of extraction with ether and concentrated sulphuric acid seem to have been applied for their isolation.

As has been discussed in connection with the preparation of tungstotitanic acid, there is always the strong possibility that metatungstic acid will be prepared during the preparation of a substituted heteropoly acid.[41,44] Conditions which cause the formation of metatungstates from paratungstates must be avoided or suppressed as much as possible.

Methods based on those which had been modified in the preparation of the tungstotitanic compounds, were applied on an attempt to prepare the iron anologues, namely $H_q\left[Fe(W_2O_7)_6\right].xH_2O$ and $H_q\left[Fe(W_2O_7)_5O\right].xH_2O$.

Separation.

Separation of the free acid was attempted by the Drechsel method[28], when if a heteropoly acid of the limiting series is present, the mixture separates into three layers:

(1) ether-water layer (topmost).

(2) acid-aqueous layer (middle).

(3) heavy oily layer, ether addition compound of the heter--opoly acid (bottommost).

The separation of the free acid was also effected through decomposition of the lead salt with sulphuretted hydrogen in alcoholic solution[48].

Analysis.

About 50 drops of the ether oil were placed in a weighed platinum crucible, heated over a very small flame until quite dry and then ignited to a low red heat for twenty minutes, cooled and weighed. When constant, this gives the weight of the mixed oxides Fe_2O_3 and WO_3. The mixed oxides are now fused with sodium carbonate, the melt extracted with hot water, the ferric oxide filtered off and redissolved in hydrochloric acid. The iron is reprecipitated with ammonia and ignited to Fe_2O_3 which is weighed. If the tungsten must also be estimated, it is precipitated from the filtrate as mercurous tungstate or cinchonine tungstate and ignited to the oxide WO_3.

PRACTICAL DETAILS OF THE PREPARATIONS.

It seemed possible that the best source of ferric iron for the purpose would be a salt containing iron as part of a negative complex radicle, for example an alkali ferri-

-fluoride, since in the tungsten complexes of the limiting series the additional constituent atom is undoubtedly neg--ative in character. e.g. B, Si, P etc..

In order that the anticipated compound contains Fe_2O_3: WO_3 in the ratio 1:24 (12-tungstoferrite) or 1:20 (10-tungsto-ferrite) 12 molecule normal sodium tungstate or $\frac{12}{7}$ molecule sodium paratungstate $3Na_2O.7WO_3$ must react with at least one molecule of potassium ferrifluoride, if the hydrolysis of the ferrifluoride is quantitative. In the first preparations, twice the molecular proportion of potassium ferrifluoride was added, in order that an adequate proportion of ferric iron would be present.

(1) 25 grams normal sodium tungstate in 400 ml water were acid--ified to p_H 6.4 with nitric acid. This solution of sodium paratungstate was treated with 4.325 gram of potassium ferri--fluoride in solution, added dropwise. When the solution was stable to strong acidification, it was treated with ether and strong sulphuric acid and the ether oil purified and analysed. 0.9050 gram of the mixed oxides contain 0.0127 gram of Fe_2O_3 i.e. $Fe_2O_3 : WO_3 :: 1:43.90$

This ferrifluoride saturation was repeated several times and the ether oil always contained $Fe_2O_3 : WO_3$ in the neighbourhood of 1:40. A brownish white residue was thrown out of solution, which when tested was found to contain a large proportion of iron. Hence loss of hydrofluoric acid must have taken place without accompanying absorption of iron. This would necessarily give rise to metatungstate and on extraction, metatungstic acid. On one occasion excess fluoride as sodium

fluoride was added to the stabilised mixture, in an attempt to keep the iron in solution. The ether oil was found to contain $Fe_2O_3:WO_3::1:41.70$.

(2) Because of the slight solubility of potassium ferrifluoride, ferric fluoride was tried as a saturating agent. This salt was prepared as a violet crystlline salt by solution of iron wire in hydrofluoric acid. It dissolves in water and hydrolyses only on long standing. The method of preparation, purification and analysis were carried out as before. The sample of ether oil gave $Fe_2O_3:WO_3::1:160$.

(3) Freshly prepared potassium ferrifluoride was used as a saturating agent. This was done by adding 1 ml ferric chloride solution to 1 ml potassium fluoride solution (the solutions containing $FeCl_3:KF::1:6$) together to the boiling sodium para--tungstate solution. The extracted ether oil contained $Fe_2O_3:WO_3::1:131:9$.

(4) Dropwise addition of ferric fluoride solution to sodium paratungstate solution containing sodium fluoride was carried out. It was hoped by this method to overcome the disadvantage due to the small solubility of alkali ferrifluorides, by "preparing" the alkali ferrifluoride in solution. The propor--tions used were $FeCl_3:\frac{12}{7}(3Na_2O.7WO_3)::2.3gr.:25gr.$ The solution was stable and was extracted in the usual way. The ether oil contained $Fe_2O_3:WO_3::1:74.5$.

(5) Using ferric alum to saturate the alkali paratungstate, in the proportions of 6.84 gr. alum to 25 gr. normal sodium tungstate, and omitting fluoride from the preparation, samples

of ether oil were prepared which on analysis gave

$Fe_2O_3 : WO_3 :: 1 : 46.43$; $1 : 92.69$; $1 : 113.0$.

(6) Using ferric nitrate as saturating agent, in the proportions $2Fe(NO_3)_2 \cdot 9H_2O : \frac{12}{11}(3Na_2O \cdot 7WO_3) :: 5.73$ gr. : 25gr. a saturation was carried out as follows:

A solution of 25 grams of normal sodium tungstate in 400 ml water acidified to p_H 6.4 with nitric acid was kept boiling and mechanically stirred while 5.8 grams of ferric nitrate dissolved in 500 ml water, was added to the boiling solution at the rate of two drops per minute. As each drop was added a yellowish-white precipitate was formed, redissolving almost at once. When all was added the mixture was divided into two portions, and to one portion 3 grams sodium fluoride in aqueous solution was added. Then both portions were concentratedto small bulk, and both were extracted with ether and sulphuric acid in the Drechsel manner.

Ether oil extracted from the first solution (no fluoride present).

1.2395 grams mixed oxides contain 0.0395 gram Fe_2O_3

i.e. $Fe_2O_3 : WO_3 :: 1 : 20.95$.

Ether oil extracted from second solution (fluoride present).

0.9076 gram mixed oxides contain 0.0332 gram Fe_2O_3

i.e. $Fe_2O_3 : WO_3 :: 1 : 20.80$.

Thus the presence of fluoride is of little account. The iron-content of the ether oil is much higher when ferric nitrate is used as saturating agent than with any other ferric compound previously tried. The above figures correspond to an acid of the type $H_q\left[FeO(W_2O_7)_5\right] \cdot aq.$ but when this method of saturation was repeated ether oils containing an even higher

proportion of iron were obtained.

Results of analyses of samples, prepared by ferric nitrate saturation as above, are as follows:

$Fe_2O_3:WO_3$ ::1:19.50; 1:17.56; 1:20.38; 1:17.73; 1:21.55; 1:20.52 and 1:19.03.

Ferric nitrate, as shown by test with metatungstic acid, is not extractable with ether and sulphuric acid. Ferric chloride might have provided an equally suitable saturating agent, but the slight risk of extracting ferric chloride in strongly acid solution would be involved. Therefore the samples of ether oil whose analyses figures are shown above must contain iron in the form of heteropoly complex, but may contain metatungstic acid as well. These samples were all deep amber incolour, and were clear on extraction, showing no tract of emulsification. Yet the figures vary so widely that there can be no doubt that a single compound is not being produced.

It had been found that with some extractions of the ether oil, emulsification of the whole took place, with the result that the ether oil took longer to separate out. When this happened, specimens containing $Fe_2O_3:WO_3$::1:60.6; 1:42; 1:139 were formed. The longer the ether oil took to separate the less was the proportion of iron in it. An example of this progressive decomposition is shown by analysis of three consecutive samples of ether oil from the same preparation.

First Sample, deep amber after purification by reprecipitation with ether from alcoholic solution:

1.4456 gram mixed oxides contain 0.0546 gram Fe_2O_3; $Fe_2O_3:WO_3$::1:17.56

Second sample, paler amber, as above.

0.7443 gram mixed oxides contain 0.0186 gram Fe_2O_3, $Fe_2O_3 : WO_3$ :: 1 : 21.37.

Third sample, yellow, as above.

1.1060 gram mixed oxides contain 0.0225 gram Fe_2O_3, $Fe_2O_3 : WO_3$ :: 1 : 33.23.

Attempts to eliminate conditions which produced emulsi-
-fication led to no definite conclusions.

Then it was found that if more than twice the molecular proportion of ferric nitrate was used, the preparation always emulsified on extraction, and the ether oil when it separated contained less iron than specimens from preparations containing the twice molecular proportion.

From all of these preparations a small amount of a brownish sludge comes out towards the completion. Some of it was filtered off, dried and analysed, and found to contain $Fe_2O_3 : WO_3$ in the following ratio: 1 : 3.21. This might be a ferric salt of a tungstoferric acid, so an exact analysis of the brown sludge from a ferric nitrate saturation was made. The material was dried over calcium chloride.

	(a)	(b)
Weight of ferric oxide	15.10%	15.30%
Ignition loss	13.80%	14.00%

Estimation of tungstic oxide shows that only ferric oxide, tungstic oxide and water were present in the compound . The compound $3Fe_2O.10WO_3.25H_2O$ or $2Fe_2H[Fe(WO_4)_5].12H_2O$ requires 14.77% Fe_2O_3 and 13.84% H_2O. This corresponds to the above analysis, and points to there being a heteropoly compound of this type in solution. Normal ferric tungstate (anhydrous) requires 18.62% Fe_2O_3, and the above compound contains 17.65% in the anhydrous

state. Normal ferric molybdate was obatined by Marckwald as $Fe_2(MoO_4)_3.4H_2O$ [76] by mixing two molecular proportions of ferric chloride with three molecular proportions of sodium molybdate Na_2MoO_4, as a brownish-yellow amorphous precipitate. When sodium paramolybdate was used in place of the normal molybdate, a yellow precipitate of $Fe_2O_3.5MoO_3.xH_2O$ with varying water content was formed. In preparation of the ammonium salt of molybdoferric acid, $3(NH_4)_2O.Fe_2O_3.12MoO_3.20H_2O$ [76], the pentamolybdate separates first and must be removed.

The brown residue above is, therefore, probably a ferric tungstoferrite of the pentamolybdate type. It is insoluble in water and slowly decomposed by mineral acids with formation of a ferric salt and precipitation of hydrated tungstic oxide.

There is no reason to suspect from any of the isolated products that a tungstoferric acid of the type $H_9[Fe(W_2O_7)_6]xH_2O$ or any of its salts are being produced in the described methods of preparation, but rather that a mixture of a lower complex heteropoly compound of ferric iron and tungsten is being formed, along with different proportions of metatungstic acid. It may be that the metatungstic acid is being produced exclusively during the extraction stage, by decomposition of the heteropoly complex in the strongly acid solution. It has been shown conclusively above that at least a portion of the metatungstate is produced in this way. The extracted acid of composition $Fe_2O_3 : WO_3 :: 1:18$ on an average, is surprisingly stable in aqueous solution. The dilutesolution can be evaporated repeatedly to small bulk

with only a very small separation of hydrated tungstic oxide which is almost free from iron.

Attempt to eliminate metatungstic acid.

The proportions used in the attempted preparations of the heteropoly compound from ferric nitrate and sodium tungstate were originally $2Fe(NO_3)_3 \cdot 9H_2O$: $12Na_2WO_4$ or 5.73 grams: 25 grams i.e. twice the molecular proportion of ferric nitrate necessary for the production of 12-tungstoferric acid $H_9[Fe(W_2O_7)_6]aq$.. Thus just enough ferric nitrate was added for the formation of the 6-tungstoferric acid $H_9[Fe(WO_4)_6] \cdot aq$. When ferric nitrate was used in this proportion emulsification took place on extraction, and it was found that the least amount of ferric nitrate necessary for stabilisation, and that gave the cleanest extractions with ether and sulphuric acid, was in the proportion of 4.5 grams : 25 grams sodium tungstate. From these proportions it is not possible that the extracted ether oil contains Fe_2O_3:WO_3 in a higher ratio than 1:15.3. Yet the addition of more ferric nitrate causes emulsifi-cation, and the resulting ether oil contains even less ferric oxide. Thus metatungstic acid must be being produced in the preparation as well as in the extraction. This can only be ex-plained by assuming incomplete hydrolysis of the ferric nitrate with consequent slow acidification of the alkali paratungstate solution. Thus, even if it were extractable with ether and sul-phuric acid, a pure sample of the acid containing Fe_2O_3:WO_3::1:12 i.e. the substituted acid of the paratungstate type $H_9[Fe(WO_4)_6] \cdot xH_2O$, could not be produced by any of the methods so far employed.

Preparation of 6-tungstoferric acid. $H_9[Fe(WO_4)_6]\cdot xH_2O$.

An attempt was made to produce the pure acid by saturation of the boiling alkali paratungstate solution with ferric hydroxide and concurrent slow acidification of the mixture with very dilute mineral acid.[27] It was hoped by this means to overcome the possibility of the presence of free acid at any time which would attack the alkali paratungstate.

The conditions of the preparation are as follows: To 25 grams normal sodium tungstate in 400 ml water set to p_H 6.4 by acidification with nitric acid, in the cold, a quantity of ferric hydroxide which had been freshly precipita-ted with ammonia from ferric chloride solution, was added. Ferric hydroxide from 6 grams anhydrous ferric chloride was sufficient for the saturation. The mixture was heated and stirred mechanically, while dilute nitric acid (0.02N) was added drop by drop in amount exactly sufficient to reduce the Na_2O; WO_3 ratio from 3:7, i.e. paratungstate, to 3:12, i,e. metatungstate. At this stage the solution had become stable to acidification with concentrated acid.

The first preparation which was carried out on these lines was divided into two portions:

First portion. Extracted with ether and sulphuric acid. The ether oil gave on analysis these figures:

1.1324 grams mixed oxides contain 0.0361 gram Fe_2O_3; $Fe_2O_3 : WO_3 :: 1 : 21.6$

Second portion. Precipitated from solution with guanidine hydrochloric solution, and the yellow well-defined crystalline substance analysed:

1.3787 grams mixed oxides contain 0.0747 gram Fe_2O_3; $Fe_2O_3 : WO_3 :: 1 : 12.02$

A second guanidine salt prepared in the same way was analysed; 0.5281 gram mixed oxides contain 0.0290 gram Fe_2O_3; $Fe_2O_3 : WO_3 :: 1 : 11.87$.

Thus the complex acid which exists in solution as prepared by this method is the substituted paratungstic acid $H_9[Fe(WO_4)_6]$ aq. and strong acidification during extraction decomposed it with production of metatungstic acid, in which apparently it is soluble to a certain maximum extent, namely 1:18.

Isolation of the acid, $H_9[Fe(WO_4)_6] \cdot xH_2O$.

The next step was to eliminate the "strong acid" method of extraction. The method that Forcher[48] had used to isolate metatungstic acid was applied.

The balanced mixture from a preparation using twice the molecular proportion of ferric nitrate, or 5.73 grams to 25 grams normal sodium tungstate, was concentrated to small bulk (50-80 ml) and lead nitrate was added to the hot solution, precipitating a bright brown crystalline substance. This was filtered off, dried in air, suspended in water and sulphuretted hydrogen passed into the suspension for from two to three hours. The suspension turned first deep brown and eventually black. The filtrate from the lead sulphide was concentrated in a vacuum des-iccator to dryness. The crystalline mass was then treated with alcohol, in which it partially dissolved to a deep amber solution. When ether was added to a sample of the alcoholic solution a sticky buff-coloured substance was precipitated, and no ether-oil was produced. Thus the bulk of the compound was not of the

metatungstate type. The amber alcoholic solution was evaporated in a vacuum desiccator to a very viscous liquid, and eventually crystals appeared. They were yellow and very soluble, and it was difficult to separate them from the mother liquor. A sample was obtained, however, and analysed for iron and tungsten.

0.2127 gram mixed oxides contained 0.0118 gram Fe_2O_3; $Fe_2O_3:WO_3$:: 1:12.16.

This was repeated:

A balanced mixture of sodium salts from 50 grams normal sodium tungstate saturated with ferric hydroxide (as described above) was concentrated and treated cold with excess lead acetate solution. The lead salt, pale brown in colour, was dried in air, suspended in alcohol and exhaustively treated with sulphuretted hydrogen. The alcoholic extracts were evaporated almost to dryness, taken up in 15 ml alcohol and filtered to remove a small amount of brown residue. The dark red liquid was mixed with a large excess of dry ether, which precipitated a semi-solid mass of similar colour. Part of this was placed in a platinum crucible and analysed.

0.8454 gram of mixed oxides contain 0.0448 gram Fe_2O_3; $Fe_2O_3:WO_3$:: 1:12.30.

Thus the acid prepared through the lead salt contains iron and tungsten in proportions required by the formula $H_9[Fe(WO_4)_6]xH_2O$.

As has been mentioned the crystalline material produced by evaporation of the filtrate from the lead sulphide, prepared

by saturation with sulphuretted hydrogen in aqueous solution, was only partly soluble in alcohol. The in--soluble residue was colloidal in nature; it was filtered off and dried to a dark brown "resin-like" material. Analysis showed it to contain $Fe_2O_3:WO_3::1:5$. It con--tained nitrate ion as well as iron and tungsten, and probably contained basic ferric nitrate. The presence of ferric nitrate points to hydrolysis, possibly due in the first instance to the formation of a compound similar to $PbO.4WO_3.Pb(NO_3)_2.10H_2O$.[79] Treatment of this double salt with sulphuretted hydrogen would liberate nitric acid as well as the heteropoly acid, so in order to eliminate hydrolysis, the treatment of the lead salt suspension with sulphuretted hydrogen was carried out in alcoholic solution.

Thus treatment of the lead salt of the heteropoly acid in non-aqueous solution with sulphuretted hydrogen produces the free acid of formula $H_q\left[Fe(WO_4)_6\right].xH_2O$.

Properties.

The free acid is obtained in small yellow crystals, which fuse to a black mass on gentle heating, give up water and cool to a dark brown solid.

The crystals are very soluble in water, and treatment with caustic alkali decomposes them with liberation of ferric hydroxide, and solution of the tungsten as alkali tungstate.

SALTS OF TUNGSTOFERRIC ACID.

Ammonium salt.

Rosenheim and Schwer[64,65] had described a salt of formula

$(NH_4)_4H_5[Fe(WO_4)_6]$.aq. as already stated on page 47.

A hot balanced mixture, prepared by saturating sodium paratungstate solution with ferric nitrate solution, was div--ided into two portions. The first portion was treatedwith saturated ammonium chloride solution and the second with saturated ammonium nitrate solution. No precipitate came down in either case, but on cooling the ammonium chloride saturation, yellow crystals appeared which were heavily contaminated with ammonium chloride. These crystals appeared to be dichroic, and on analysis gave Fe_2O_3 : WO_3 :: 1 : 7.39.

From the filtrate a deeper orange finely crystalline substance separated, in very small quantity. On analysis this substance was found to contain Fe_2O_3 : WO_3 :: 1 : 11.2.

On cooling and concentrating the ammonium nitrate saturation, fine yellow crystals separated, which were soluble in water to a slightly turbid solution. Analysis gave these figures:

Weight of ignited residue	0.9432 gram.
" " Fe_2O_3	0.0446 gram.
" " WO_3 (separate estimation)	0.8732 gram.

Fe_2O_3 : WO_3 :: 1 : 13.50.

This salt contained some impurity, probably a small amount of sodium salt.

These salts separated in very small quantities, and in an impure state, so that complete analysis have not yet been carried out. There can be little doubt, however, that they are derivatives of the acid $H_6[Fe(WO_4)_6]$.aq.

Potassium salt.

The potassium salt was described by the same authors[65], who prepared it in the same way as the ammonium salt, and ascribed to it a similar formula: $K_4H_5[Fe(WO_4)_6]aq.$

Attempted preparation of this salt by treatment of the balanced mixture with potassium chloride solution, led to the separation of a minute amount of a yellow crystalline solid. On concentration a dark orange red liquid, resulted, from which potassium nitrate separated and which was stable to acidification, but no further crystals separated.

Guanidine salts.

The guanidine salt $(CN_3H_6)_4H_5[Fe(WO_4)_6].aq.$ was prepared by Rosenheim and Schwer[65] in a manner similar to the potassium and ammonium salts.

Reagent: 50 grams guanidine carbonate were neutralised with hydrochloric acid to methyl orange, and made up to 250 ml solution with distilled water. 20-25 ml of this reagent are necessary for complete precipitation from a 25 grams normal sodium tungstate quantity of balanced mixture.

In the earlier preparations of the guanidine salts, it was found that as soon as the guanidine hydrochloride solution was added to the balanced mixture, a plae buff amorphous compound was precipitated. After filtration, the filtrate which was still yellow, and saturated with guanidine hydrochloride slowly deposited a definitely crystalline yellow material, leaving the solution colourless.

Analyses of the first precipitated compounds gave results for $Fe_2O_3:WO_3::$ of from 1:22 to 1:37.54. Never did analyses

of two of these compounds agree. Guanidine was estimated by the Kjeldahl method in compounds whose $Fe_2O_3:WO_3$ ratio was as low as 1:24.

These guanidine salts were insoluble and could not be recrystallised. A specimen containing $Fe_2O_3:WO_3::1:21$ was analysed completely.

Percentage of	guanidine oxide	12.96%
"	water (by difference)	3.98%
"	ferric oxide	2.54%
"	tungstic oxide	80.45%
Total.....		99.93%

Empirical formula: $3(CN_3H_6)_2O.Fe_2O_3.21WO_3.24H_2O$ or

$$(CN_3H_6)_3H_6\left[FeO(W_2O_7)_6\right].9H_2O.$$

Another specimen had an empirical formula:

$$(CN_3H_6)_4H_5\left[FeO(W_2O_7)_5\right].8H_2O.$$

It is very probable that these compounds are not simple salts, but mixtures of guanidine metatungstate with guanidine 6-tungstoferrite.

The definitely crystalline second fraction, which cannot be crystallised except from the mother liquor was found to be authentic guanidine 6-tungstoferrite.

<u>Analyses:-</u>

(1) Percentage	guanidine oxide	11.12%
"	water	4.13%
"	ferric oxide	4.80%
"	tungstic oxide	80.00%
Total.....		100.05%

Empirical formula: $(CN_3H_6)_3H_6\left[Fe(WO_4)_6\right].4H_2O$

(2) Percentage guanidine oxide 14.76%

" water 3.54%

" ferric oxide 4.42%

" tungstic oxide 77.25%

Total..... 99.97%

Empirical formula: $(CN_3H_6)_4H_3[Fe(WO_4)_6].2H_2O.$

(3) Percentage guanidine oxide 13.37%

" water 4.49%

" ferric oxide 4.41%

" tungstic oxide 77.26%

Total..... 99.53%

Empirical formula: $3.5(CN_3H_6)_2O.Fe_2O_3.12WO_3.10H_2O.$

(4) Percentage guanidine oxide 12.13%

" water 8.73%

" ferric oxide 4.35%

" tungstic oxide 74.91%

Total..... 100.12%

Empirical formula: $3.5(CN_3H_6)_2O.Fe_2O_3.12WO_3.16.5H_2O.$

Thus the authentic guanidine salt of the acid $H_6[Fe(WO_4)_6].aq$ can be obtained by fractional crystalisation of a mixture of guanidine salts, the mixture probably containing guanidine meta--tungstate and guanidine 6-tungstoferrite only.

When a preparation from a ferric hydroxide saturation was treated with the requisite amount of guanidine hydrochloride solution one compound, deep yellow and crystalline, came down on standing. There was no second fraction. Complete analysis of

this compound gave these results:

• Percentage	guanidine oxide	9.68%
"	water	10.38%
"	ferric oxide	4.35%
"	tungstic oxide	76.12%
Total.....		100.53%

Empirical formula: $2.5(CN_3H_6)_2O.Fe_2O_3.12WO_3.22H_2O$.

Thus more than one guanidine salt of $H_aq[Fe(WO_4)_6]$.aq. exists.

Pyridine salt.

This compound was prepared in a similar way to the guanidine salts.

It was found that when pyridine hydrochloride was added to the balanced mixture, the whole of the tungsten complex in solution was precipitated. Thus the difference in solubility between pyridine metatungstate and pyridine 6-tungstoferrite is not marked. Pyridine salts were thereforeprepared from ferric nitrate saturation preparations to verify the relative amounts of Fe_2O_3: and WO_3 in solution. It was found that the pyridine hydrochloride brings down a compound which contains Fe_2O_3:WO_3 in the ratio of 1:15 approximately, which is the proportions added.

The pure pyridine salt can be prepared only from ferric hydroxide saturation preparations. It comes down as an oil and gradually crystallises out. It was filtered, drained, and dried in air.

Analysis.

Percentage water	19.57%

Percentage guanidine oxide		18.42%
"	ferric oxide	2.99%
"	tungstic oxide	58.91%
Total.....		99.89%

Empirical formula: $5.5(C_5NH_6)_2O.Fe_2O_3.12WO_3.57H_2O.$ or

$(C_5H_6N)_6H_2\left[Fe(WO_4)_6\right].27.5H_2O.$

THE MECHANISM OF FORMATION OF 6-TUNGSTOFERRIC ACID.

The free heteropoly acid of iron and tungsten which has been prepared, and its derivatives, are of the paratungstate type. The free acid is denoted by the formula $H_9\left[Fe(WO_4)_6\right]$.aq.,[74] a derivative of the hypothetical "paratungstic acid" $H_{10}\left[H_2(WO_4)_6\right]$.aq.[18]

Rosenheim[65] gives no information as to the relative amounts of alkali paratungstate and ferric chloride used in his preparations of these compounds, nor does he express any opinion as to the nature of the reaction involved.

Since ferric chloride (or ferric nitrate) solutions are quite acid in reaction and sodium paratungstate is approximately neutral, it seems probable that the main action is the removal of alkali from the paratungstate by free acid liberated by the hydrolysis of ferric chloride in hot dilute neutral solution, with resulting saturation of the tungstate anion with ferric hydroxide.

Rosenheim's[65] formula of the salts: $4K_2O.Fe_2O_3.12WO_3.aq.$ and $4(NH_4)_2O.Fe_2O_3.12WO_3.aq$ would require the removal of two equivalents of alkali per molecule:-

$$5K_2O.12WO_3 \longrightarrow 4K_2O.Fe_2O_3.12WO_3$$

This is equivalent to two-thirds molecule of ferric chloride, assuming

complete hydrolysis of the latter. The conversion of alkali tungstate of the type $5K_2O.12WO_3$ to metatungstate of the type $3K_2O.12WO_3$ requires the removal of 4 equivalents of alkali. When this is done by the addition of mineral acid at a rate sufficiently slow to allow the tungstic oxide set free to be redissolved in the residual paratungstate, the resulting sol--ution is stable to strong acidification and gives the character--istic ether addition compound of metatungstic acid on addition of ether. Rosenheim and Schwer did not apply the Drechsel method to their balanced solutions, possibly assuming that the tungsto--ferric acid and its salts would behave like the paratungstates and decompose with precipitation of hydrated tungstic oxide.

As has already been stated, Britton and German[73] have shown that there are compounds of formulae $3Na_2O.7WO_3$ and $5Na_2O.12WO_3$, the former existing in solution of p_H 6.4 the latter in solution of p_H 6.1. The literature is not clear as to which of these is the paratungstate of sodium.

The solutions of sodium paratungstate which have been used in the ferric nitrate saturation preparations, were ad--justed to p_H 6.4 and thus contained the compound $3Na_2O.7WO_3$. Since iron is tervalent there is a possibility than an analogue of 12-tungstoboric acid might exist. This would have the formula $H_9[Fe(W_2O_7)_6].aq.$, and would be of the metatungstate type, capable of extraction from its salts with ether and sulphuric acid.[28]

During the earlier preparations it was repeatedly observed that the balanced mixture of sodium salts was stable to

acidification and gave an ether addition compound containing iron when extracted by the Drechsel method.[28] The extracted acid varied widely in iron content, giving values of $Fe_2O_3 : WO_3$ from 1:20 to 1:120. In all cases, at least two molecules of ferric salt were added per molecule of sodium paratungstate, and in each case a permanent precipitate remained at the end of the preparation.

Tests to determine the relationship between the point at which the precipitation became permanent and the proportion of ferric salt added, showed that in four cases this occurred when ferric salt corresponding to 5.25, 4.85, 5.37, 4.90 equivalents of acid had been added. The reaction therefore requires for com-pletion more than the two equivalents of acid required by Rosenheim's formulation of the potassium and ammonium tungsto-ferrites.

The variation in hydrogen ion concentration during saturation has also been followed. Sodium paratungstate has as stated above,[73] a p_H of about 6.4 in approximately 6% solution. On conversion to sodium metatungstate the p_H falls to 5.4-5.8, and it is reasonable to suppose that sodium salts of 12-heteropoly acids would give values in the same region. For the substituted paratungstic acids, since these should be stronger than para-tungstic acid itself, the values should be intermediate between H 6.4 and p_H 5.4.

Saturation of sodium paratungstate with ferric nitrate.

25 grams normal sodium tungstate in 400 ml water set to p_H 6.4 with nitric acid. 4.5 grams ferric nitrate ($Fe(NO_3)_3 . 9H_2O$), which is equivalent to 4.72 equivalents of acid, were used for

saturation. This quantity of ferric nitrate was used in solution in 550 ml water.

After 400 ml solution (3 grams ferric nitrate) added pH c 6.4.

" 500 ml " (4 " " ") " pH c 6.0.

" 550 ml " (4.5 " " ") " pH c 4.0

There was a very slight permanent precipitate at the end, and the solution was stable and extractable by the Drechsel method.[28]

The ether addition compound gave Fe_2O_3:WO_3::1:17.5.

After repurification..... 1:18.5.

Repetition of this gave similar results, the final pH being 4.2-4.0, and the extracted acid containing Fe_2O_3::WO_3::1:18.0.
(4.72 equivalents of acid)

This value appears to be constant, and is midway between that required for production of "the substituted paratungstic acid" $H_9[Fe(WO_4)_6]$.aq. and that required for production of "the substituted metatungstic acid" $H_9[Fe(W_2O_7)_6]$.aq.. The extracted acid may thus be regarded as either an equimolecular mixture of these two acids, or as a mixture of $H_9[Fe(WO_4)_6]$.aq. and metatungstic acid $H_{10}[H_2(W_2O_7)_6]$.aq. in the ratio of 2:1.

Since there is no permanent precipitate at the end point, it is reasonable to assume that the balanced mixture of sodium salts, contains all the added iron in complex form. This is proved by testing the mixture with potassium thiocyanate solution in absence of mineral acid, when the test is negative. In this case, Fe_2O_3:WO_3 for the balanced mixture should be 1:15.3, since these are the proportions added.

Since many preparations give values much below this, it is clear that metatungstic acid must enter into some, at any rate.

No evidence has been found of the acid $H_9[Fe(W_2O_7)_6]$.aq.

nor its salts, and it is probable that only $H_9[Fe(WO_4)_6]\cdot aq$ and $H_{10}[H(W_2O_7)_6]\cdot aq$ are present at any time. It is clear that metatungstic acid is formed both in the preparation and in the extraction, and that in presence of metatungstic acid tungstoferric acid is capable of extraction by the Drechsel method.[28]

On the basis that sodium paratungstate is formulated $5Na_2O.12WO_3$, the saturation may be expressed as follows:

(1) $5Na_2O.12WO_3 + \frac{4}{3}Fe(NO_3)_3 = \frac{2}{3}(3Na_2O.Fe_2O_3.12WO_3) + \frac{1}{3}(3Na_2O.12WO_3) + 4NaNO_3$.

This gives $Fe_2O_3:WO_3$ in the ratio of 1:18, and $\frac{4}{3}(Fe(NO_3)_3\cdot 9H_2O) = 3.82$ grams

Repeated saturations show that stability is not reached below 4 grams ferric nitrate.

Alternatively:

(2) $\frac{12}{7}(3Na_2O.7WO_3) + \frac{10}{7}Fe(NO_3)_3 = \frac{5}{7}(3Na_2O.Fe_2O_3.12WO_3) + \frac{2}{7}(3Na_2O.12WO_3) + \frac{30}{7}NaNO_3$.

This gives $Fe_2O_3:WO_3$ in the ratio of 1:16.8, and $\frac{10}{7}(Fe(NO_3)_3\cdot 9H_2O) = 4.09$ gr.

This equation is probably the correct one as regards the course of saturation. That the ratio $Fe_2O_3:WO_3$ is nearer 1:18 than 1:16.8 is probably due to the loss of iron in the period before the ether addition compound layers out completely, a matter of minutes at least.

If saturation were complete, the $Fe_2O_3:WO_3$ ratio for the balanced sodium salts would be 1:12. Then:

(3) $\frac{12}{7}(3Na_2O.7WO_3) + 2Fe(NO_3) + \frac{6}{7}H_2O = 3Na_2O.Fe_2O_3.12WO_3 + \frac{30}{7}NaNO_3 + \frac{12}{7}HNO_3$

$2(Fe(NO_3)_3\cdot 9H_2O) = 5.73$ grams.

In this case, hydrogen ion will be set free, owing to the lack of balance between the ferric ion and the tungstic oxide, and this may either:

(a) form a more acid sodium salt,

(b) liberate free tungstoferric acid,

(c) decompose the latter with formation of metatungstic acid.

Since the saturation is essentially a hydrolysis process, decom-
-position of ferric nitrate will take place until the p_H of the solution has fallen below 3.

Saturation of potassium paratungstate with ferric nitrate.

This was run for purposes of comparison.

30.8 grams potassium tungstate ($K_2WO_4.2H_2O$) on treatment with 99.7 ml normal nitric acid gives a solution of p_H 6.4 in a volume of 400 ml. The composition of the salt present corresponds closely to $5K_2O.12WO_3$ or potassium paratungstate. Saturation of this sol-
-ution with 4.0 grams ferric nitrate ($Fe(NO_3)_3.9H_2O$), which is equivalent to 4.19 equivalents of acid, gave the following p_H values:

After addition of 1 gram ferric nitrate in solution	pH c 6.2
" " " 2 " " " " "	pH c 4.8
" " " 3 " " " " "	pH c 4.8
" " " 4 " " " " "	pH c 4.6

The resulting solution was stable to acidification and extractable by the Drechsel method.[28] The drop in pH after addition of the second gram of ferric nitrate shows that the buffer action of potassium paratungstate is much less marked than that of sodium paratungstate, but here again stability is reached only when the amount of ferric salt added is equivalent to 4 equivalents of acid. i.e. the amount of acid necessary to convert $5K_2O.12WO_3$ to $3K_2O.Fe_2O_3.12WO_3$.

This difference in behaviour between potassium and sodium tungstate is possibly due to the fact that thelatter, in solution at least, is really $3Na_2O.7WO_3$, and is thus the more alkaline salt. The supplementary Na_2O will be set free in the change from $3Na_2O.7WO_3$ to $3Na_2O.Fe_2O_3.12WO_3$.

30 grams normal sodium tungstate in 400 ml solution were set to pH 6.4 with nitric acid and saturated with 4.93 grams ferric nitrate (9-hydrate) dissolved in 600 ml water. 4.93 grams ferric nitrate is equal to $\frac{3\ 0}{7}$ equivalents of acid.

After addition of 100 ml solution (0.822 gram ferric nitrate) pH c 6.4
" " " 200 ml " (1.644 " " ") pH c 6.4
" " " 300 ml " (2.466 " " ") pH c 6.4
" " " 400 ml " (3.288 " " ") pH c 6.4
" " " 500 ml " (4.110 " " ") pH c 6.4
" " " 550 ml " (4.521 " " ") pH c 6.4
" " " 600 ml " (4.932 " " ") pH c 5.8

The solution is stable to strong acid, contains a very slight precipitate and emulsifies on extraction. The final pH in this case corresponds closely with that found in the ferric hydroxide satura--tions.

As will be seen from the pH values quoted sodium paratung--state acts as a buffer of pH 6.4 up to the addition of 3 grams ferric nitrate, the next gram only lowers the pH from 6.4 to 6.0 and the final 0.5 gram causes a sharp fall from pH 6.0 to pH 4.0. During the addition of the final half gram, the reaction mixture is evidently in a state of unstable equilibrium. While most preparations run with a neglegible amount of precipitate formation, in some cases extensive precipitation of a material rich in iron occurs. In such cases the mother liquors contain less 6-tungstoferrits and a higher proportion of metatungstic acid and give values for Fe_2O_3:WO_3 much below the 1:18 average.

In the later stages of saturation, hydrolysis of the ferric

nitrate becomes increasingly incomplete. Since the precipitate formed is richer in iron than the 1:12 proportion prevailing in the mother liquor, nitric acid must be set free, and it is pro-bable that the metatungstic acid arises from the interaction of this with the already formed 6-tungstoferrite. That mineral acid has this effect is shown beyond doubt in the decreasing proportion of iron in successive fractions of the ether addition compounds separated by the Dreschel method[28] and also by the fact that, whereas the balanced mixture containing sodium 6-tungsto-ferrite gives a negative reaction for the ferric ion with ammonium thiocyanate, the reaction becomes positive on the addition of acid.

When ferric ammonium alum was used as a saturating agent, the extracted acid gave Fe_2O_3 : WO_3 :: 1:113. Since the hydrolysis of ferric sulphate gives rise to sparingly soluble basic sulphates, with consequent loss of iron from solution and liberation of sulphuric acid, the low iron content is to be expected.

In the cases of ferric nitrate and ferric chloride, the basic salts formed are more soluble in water, and remain as a potential source of ferric hydroxide.

A ferric nitrate solution including 14 grams hydrated ferric nitrate per litre, which is rather more concentrated than the solutions used in the saturations, has a pH value of about 1.8. This corresponds to about 10 per cent hydrolysis of the ferric nitrate, and the ferric nitrate is thus in equilibrium with about $\frac{N}{100}$ nitric acid. As the reaction between alkali paratungstate and

free mineral acid to produce metatungstate is quite rapid, it is probable that part at least of the metatungstic acid formed during saturation comes from this source.

The results obtained from the hydrolytic saturation showed that this method cannot give a sodium salt of tungstoferric acid entirely free from sodium metatungstate (see equations (2) and (3) above).

The alternative method, saturation with ferric hydroxide, which results in the formation of $3Na_2O.Fe_2O_3.12WO_3$ from $3Na_2O.7WO_3$ and thus involves a reduction of the $Na_2O:WO_3$ ratio, takes place with the displacement of caustic soda from the paratungstate, thus:

(4) $5Na_2O.12WO_3 + 2Fe(OH)_3 = 3Na_2O.Fe_2O_3.12WO_3 + 4NaOH + H_2O$.

Since the substituted paratungstates exist only in solution of pH less than 6.4, the reaction will come to a standstill after liberation of a small amount of alkali.

Since the complete conversion of $\frac{12}{7}(3Na_2O.7WO_3)$ to $3Na_2O.Fe_2O_3.12WO_3$ involves the removal of $\frac{15}{7}$ Na_2O, the amount of acid necessary to balance the reaction will be $\frac{30}{7}$ equivalents. The acid must be added in such a dilution and at such a rate that it reacts only with the alkali set free in the saturation and not with the sodium paratungstate. Addition of 0.2 normal nitric acid at a rate of one drop every 40-50 seconds, gives satisfactory results.

Th (5) $\frac{12}{7}(3Na_2O.7WO_3) + 2Fe(OH)_3 + \frac{30}{7}HNO_3 = 3Na_2O.Fe_2O_3.12WO_3 + \frac{30}{7}NaNO_3 + \frac{36}{7}H_2O$

(5) $\frac{12}{7}(3Na_2O.7WO_3) + 2Fe(OH)_3 + \frac{30}{7}HNO_3 = 3Na_2O.Fe_2O_3.12WO_3 + \frac{30}{7}NaNO_3 + \frac{36}{7}H_2O$

In this case there is no free acid to cause decomposition of the sodium salt formed, the final pH being on an average between 5.8 and 5.4.

The guanidine salt precipitated from the balanced mixture of sodium salts gives $Fe_2O_3:WO_3$ ::1:12, and $Fe_2O_3:WO_3$::1:18 is thus an opti guanidine 6-tungstoferrite. The balanced mixture of sodium salts is stable to acid, but on extraction with ether emulsifies badly. In some cases the emulsion persisted for several days, but in no case was there any marked precipitation of tungstic oxide.

This is most reasonably explained on the assumption that tungstoferric acid $H_9[Fe([Fe(WO]$ .aq. does not give an ether addition compound of the type given by metatungstic acid and substituted metatungstic acids. Instead it may give an addition compound with ether similar to those formed by inorganic acids of high molecular weight, for example, $H_4[Fe(CN)_6]$ and $H_3[Co(CN)_6]$. It is found that cobalticyanic acid $H_3[Co(CN)_6]$ is appreciably extracted by the Drechsel method in presence of metatungstic acid, which makes it entirely probable that 6-tungstoferric acid has the same or even more pronounced property.

With cobalticyanic acid and ferrocyanic acid the ether addition compound, which has a sticky appearance, collects at the ether -water interface.

In the strongly acid solution, 6-tungstoferric acid loses iron to give metatungstic acid, and when the molecular pro-portion has reached 2:1, the characteristic oily layer separates. The ratio $Fe_2O_3:WO_3$::1:18 is thus an optimum equilibrium value.

The experimental evidence quoted shows that pure 6-tungsto-ferric acid cannot be prepared from the sodium salt by extraction with ether and sulphuric acid. Treatment of the lead salt in non-aqueous solution with sulphuretted hydrogen seems to be the only practicable method.

SUMMARY OF RESULTS.

Free Acid.

Tungstoferric acid of formula $H_9[Fe(WO_4)_6]$.aq. is the only iron-tungsten heteropoly acid which can be considered definite. It can be preparedpure only through decomposition of the lead salt with sulphuretted hydrogen. The other standard methods for the preparation of heteropoly tungstic acids from their sparing--ly soluble salts, for example, the action of chloroplatinic acid on the ammonium salt, the action of hydrochloric acid on the silver or mercurous salt, or of sulphuric acid on the barium salt, all expose the acid set free to the strong acid used to liberate it. Since the reaction between the sparingly soluble complex salt and the chloroplatinic, hydrochloric or sulphuric acid is necessarily slow, the free heteropoly acid is exposed momentarily to the added acid, resulting in positive ionisation of the iron and formation of meta--tungstic acid, giving a product poorerin iron than the salt used as starting material.

No analogues of borotungstic acid exists, which would be formulated $H_9[Fe(W_2O_7)_6]$.aq.

The salts.

The most definite salts are the guanidine salts of the above acid. There appears to be more than one, 3.5-basic and 2.5-basic salts of the acid $H_9[Fe(WO_4)_6]$.aq. have been prepared. The ammonium and potassium salts described by Rosenheim[65], have been found to be extremely soluble and have not been obtained pure or in sufficient quantity for analysis. It may be that they form stable supersaturated solutions.

PART 2a.

HETEROPOLY TUNGSTEN-ALUMINIUM AND TUNGSTEN-CHROMIUM COMPLEXES.

Historical survey.

Rosenheim and Schwer[74] described compounds of the type $H_a\left[M(XO_4)_6\right]$ in which $M = Fe^3$, Cr, Al, and X = W or Mo as has already been stated on page 48. They stated that the aluminium and chromium compounds hydrolyse on standing and that the ferric compound hydrolyses immediately.

A compound of formula $(NH_4)_2O.Al_2O_3.9WO_3$ was prepared by H.Daniels.[80] Compounds of this type were prepared by boiling alkali paratungstate with freshly precipitated aluminium hydroxide and were obtained by evaporation as vitreous solids. The method of preparation makes it almost certain that these products were heavily contaminated with colloidal aluminium hydroxide and were not individuals.

If the conclusions arrived at in the discussion of 6-tungstoferric acid and its derivatives are valid, there is no reason that the oxides of other tervalent metals should not give similar compounds, provided the tervalent metal has no outstanding tendency to form complex hydrated ions. This the chromium ion has, and thus difficulties in the preparation of 6-tungstochromite might be anticipated. Aluminium should behave similarily to ferric iron.

Practical details.

In order to test the properties of aluminium and chromium in this direction, a quick method was used. Although it has been shown that a pure specimen of tungstoferric acid can not be prepared by saturation of alkali paratungstate by a ferric

salt, and that a certain proportion of metatungstic acid is necessarily concurrently produced, this method, if applied to aluminium and chromium, will show whether or not a heteropoly complex of these metallic ions is being produced at all. The metatungstate formation can be cut down to a minimum by addition of small quantities of the solid salt, which prevents the addition of a solution acid by hydrolysis to the alkali para--tungstate. This was the rapid method used in attempted prepar--ation of 6-tungstoaluminate and 6-tungstochromite.

6-tungstoaluminate.

The quantities of aluminium sulphate and normal sodium tungstate used were as follows: $12Na_2WO_4 : Al_2(SO_4)_3 . 18H_2O$

6.25 gr. : 0.969 gr.

in order that the heteropoly compound would contain $Al_2O_3 : WO_3 :: 1 : 12$. 6.25 grams normal sodium tungstate were dissolved in 100 ml water and the pH adjusted to 6.4 with nitric acid. The solution was kept stirred mechanically, heated, and the solid aluminium sulphate added in six portions. Each portion produced a precipitate which dissolved to a clear solution almost immediately. After the last addition of solid there was a slight white gelatinous precipitate. When cool the solution was stable to concentrated hydrochloric acid. Guanidine hydrochloride, which should, by analogy with the iron complexes precipitate the whole heteropoly-iso-poly complex in solution on standing, was added to the stable solution. An amorphous white precipitate which came down, was washed with dilute guanidine hydrochloride solution, drained and dried in air. Analysis showed: 0.0203 gram Al_2O_3 and 0.7251 gram WO_3 in the salt.

i.e. $Al_2O_3 : WO_3 :: 1 : 15.84$.

These are the proportions which would be expected if the aluminium acts in the same way as ferric iron, see page 70. Thus there is a fair chance that 6-tungstoaluminate can be prepared as follows:

$$\frac{12}{7}(3Na_2O.7WO_3)+2Al(OH)_3+\frac{30}{7}HNO_3 = 3Na_2O.Al_2O_3.12WO_3+\frac{30}{7}NaNO_3+\frac{30}{7}H_2O$$

To 25 grams normal sodium tungstate in 400 ml water with the pH adjusted to 6.4 with nitric acid, freshly precipitated aluminium hydroxide was added in two portions. Aluminium hydroxide precipit--ated from at least twice the molecular proportion of hydrated aluminium sulphate was added. The mixture was stirred and heated and $\frac{30}{7}$ equivalents of acid were added. (10.45 ml 2.907 N nitric acid diluted to 500 ml and added slowly from a dropping funnel). When all the acid had been added, i.e. after seven days, the excess aluminium hydroxide was filtered off and the filtrate evaporated to 80 ml. The pH was now 4.0. The solution was stable to strong acidification and addition of ether to a portion ofit caused precipitation of a white "emulsion". The stable solution was divided into portions, (1) and (2) and one half of it was treated with guanidine hydrochloride solution. The microcrystalline white precipitate was filtered, washed, air-dried and analysed.

(1) Method of analysis of guanidine salt.

The salt was heated with concentrated hydrochloric acid and a little concentrated nitric acid, which was gradually removed by taking down to near-dryness with added hydrochloric acid. The solution was evaporated once or twice to small bulk, then diluted a little and cinchonine hydrochloride added in small quantities till no further precipitation. The cinchonine tungstate and excess

tungstic acid was filtered off and washed with cinchonine wash solution, (3ml cinchonine hydrochloride, 3 ml concentrated hydrochloric acid, in 100 ml solution).

Precipitate: Redissolved as completely as possible in dilute ammonia (1 vol. concentrated ammonia : 4 vols. water), the residue washed on the filter with water and the paper ignited in a platinum crucible. The tungsten is reprecipitated with dilute hydrochloric acid, and a little more cinchonine hydro--chloride, allowed to stand for a few hours, filtered and ignited to tungstic oxide.

Filtrate: Made just alkaline to methyl red with fresh dilute ammonia, washed with a little water, dried and ignited in the platinum crucible with the first precipitate.

The precipitate must be pure white, otherwise it must be fused with potassium bisulphate.

A check on the total oxides can be got by gentle ignition of another portion of the salt.

Analysis.

Salt contains 0.0585 gram Al_2O_3 and 1.6595 gram WO_3;

$Al_2O_3 : WO_3 :: 1 : 12.52$

Salt contains 0.0305 gram Al_2O_3 and 0.8630 gram WO_3;

$Al_2O_3 : WO_3 :: 1 : 12.44$

Thus the guanidine salt of 6-tungstoaluminate is formed by precipitation from the solution, so that the alkali 6-tungsto--aluminate exists in solution. The free acid has not yet been prepared.

(2) To the second portion of the balanced mixture, ammonium chloride was added in saturated solution. After heating and allowing to stand for two weeks there was still no precipitation. The ammonium salt, analogue of the Rosenheim salt[65] $(NH_4)_4H_5[Fe(WO_4)_6] \cdot xH_2O$ must be extremely soluble, or possibly tends to form stable supersaturated solutions. The complete absence of precipitate shows that there is no metatungstate in solution.

6-tungstochromite.

The quantities of chromium sulphate and normal sodium tungstate used were as follows: $12\ Na_2WO_4 : Cr_2(SO_4)_3 \cdot 5H_2O$

6.25 gr. : 0.935 gr.

in order that the heteropoly compound would contain $Cr_2O_3 : WO_3 :: 1:12$. 6.25 grams normal sodium tungstate were dissolved in 100 ml water and the pH adjusted to 6.4 with nitric acid. The solution was kept stirred and heated as before, and the solid chromiun sulphate added in six portions. When all was added the solution was dark green and was not stable to concentrated acid. A dark green gelatinous material was present and was filtered off. The filtrate was treated with guanidine hydrochloride solution which precipitated an olive green amorphous material. This was filtered, washed, dried and analysed.

Salt contains 0.0875 gram Cr_2O_3 and 1.8300 grams WO_3, $Cr_2O_3 : WO_3 : 1:13.70$

This precipitate was almost surely contaminated with gelatinous chromic oxide, or at least with the deep green gelatinous material first filtered off. The solution had not been stable to concentrated acid, so the existence of the complex was doubtful, but the method of saturation with chromic hydroxide was tried.

25 grams normal sodium tungstate was dissolved in 400 ml water and the pH set to 6.4 with nitric acid. This solution was treated with chromic hydroxide (precipitated from twice the molecular quantity of chromium sulphate with ammonia) and 30 equivalents of nitric acid added very slowly as before. The solution became dark olive green in colour. After all the acid had been added a heavy blue-green precipitate was filtered off. This precipitate contained much chromic oxide and some tungstic oxide. The filtrate was dark bottle green and stable to acid. A small portion of it was treated with ether and sul-phuric acid, when the characteristic three layers appeared. The bottom layer looked opaque, a pale green emulsion. It contained a small amount of chromium.

The bulk of the stable solution was precipitated with guanidine hydrochloride solution, and the pale green amorphous precipitate was filtered off, dried and analysed.

Method of analysis.

The guanidine salt was heated with 25% caustic soda solution till completely dissolved and then diluted till the strength was 5% and heated until the chromic hydroxide had flocculated. At this stage sulphur dioxide was passed into the solution for a short time in order to prevent any oxidation to chromate, and also since the sodium sulphite formed helps the flocculation of the chromic hydroxide.

The chromic hydroxide was filtered through a paper which had been washed within 5% caustic soda containing a little sodium sulphate, and the precipitate was washed with the same solution. The precipitate was dissolved in dilute hydrochloric acid and

and reprecipitated with ammonia using methyl red as indicator. The precipitate was ignited to chromic oxide and weighed.

The tungsten was precipitated in the filtrate with cinchonine hydrochloride and gently ignited to tungsten to oxide.

Analysis.

Salt contains 0.0193 gram Cr_2O_3 and 1.6824 gram WO_3; $Cr_2O_3 : WO_3 :: 1 : 57.10$. As expected there is much metatungstate present.

A second dark brownish green crystalline precipitate appeared in very small quantity from the filtrate. It may be the authentic salt of 6-tungstochromite, but the amount is negligible. The bulk of the chromium must have been precip--itated, from the solution, it may be as a complex of the type $Cr\left[(OH_2)_8.(CH_3COO)_3\right]$., with consequent acidification of the paratungstate to metatungstate, shown by the stability to extraction[28] of the balanced solution.

SUMMARY OF RESULTS.

Aluminium reacts in a manner similar to ferric iron, forming 6-tungstoaluminates, derivatives of the acid $H_9\left[Al(WO_4)_6\right].aq.$

Chromic chromium does not give 6-tungstochromite by the same method , or only to a very slight extent.

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